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THE

PHYSICAL REVIEW.

THE BREAKDOWN EFFECT IN BORON CONDUCTORS.

By F. W. Lyle.

WHEN across a layer of any of the ordinary insulating materials a voltage greater than a certain critical value is impressed, the familiar phenomenon of "breakdown" occurs; that is, its insulating property is lost, usually with the accompaniment of destructive physical and chemical changes. It is frequently considered that the latter are the actual causes of the disappearance of insulating power and so really constitute the "breakdown." There are, however, materials which exhibit all the electrical characteristics of the action without any such destructive accompaniment. A consideration of the results of some experiments with such substances may therefore be of interest, in which some of the similarities to the "breakdown" or "rupture" of ordinary insulations will be pointed out.

The materials exhibiting this electrical "breakdown" have, like the common insulating materials, a negative temperature coefficient of resistance. As an example of this action we may consider a slab of the element boron placed between two terminals, across which various direct current voltages can be impressed. The temperature-resistance curve of such a piece is shown in figure 1. If, at first, a low voltage is applied, only a very small current will flow, the material having at 20° C. a resistivity of 2×10^6 ohms per centimeter cube. For a few moments a gradual increase of current occurs by reason of the heating effect of the current, but a condition of current stability is soon reached and the material behaves simply as a large ohmic resistance. If now

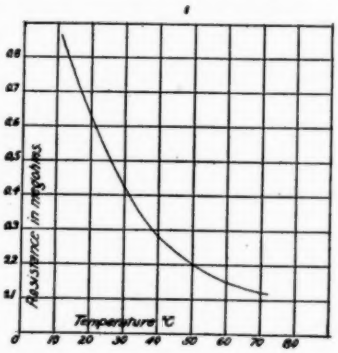

Fig. 1.

larger and larger voltages are successively applied more current will flow, but always in amount measured by milliamperes.

Finally, however, a voltage will be reached at which instability suddenly appears in the circuit. The current increases rapidly and, unless a separate resistance is in series, a short circuit of the line ensues. As is evident, the effect in the electric circuit is very much like that occurring in the breakdown of insulation. By the use of resistance, however, the current may be held at such a value that, although the piece may become red hot, further current rise is prevented. If now the circuit be opened and the boron allowed to cool, it will be found to be in the same state chemically and physically as before "breakdown."

The "breakdown" action above described can readily be shown to be due, in a general way, to the cumulative effect of internal heating on the electrical resistance of the substance. By reason of its negative temperature coefficient the latter continually decreases as the temperature of the slab rises. When this has proceeded far enough the heating becomes very rapid and the current rises quickly to the limiting value imposed by external resistance. It will be noticed that breakdown does not occur instantaneously but that time is required for it to set in, just as in the case of ordinary insulating materials.

MINIMUM VOLTAGE PRODUCING BREAKDOWN.

It might at first thought appear that breakdown will eventually take place in such materials on any voltage, however low, provided it is applied for a sufficiently long time. This, however, is not the case. There is found to be a definite value of voltage below which breakdown will never occur, no matter how long awaited. All voltages above this value produce breakdown with a rapidity depending on their excess over it. This really critical voltage may be called the "breakdown at infinite time"; its parallel in the case of common insulations is familiar. The conditions determining the value of this dividing line between voltages at which breakdown will and will not take place will now be considered.

The rise in temperature which takes place in the specimen when voltage is impressed has two effects; the increase in electrical conductivity alluded to above, and, of course, a dissipation of heat to the surroundings. The first tends to produce further temperature rise, the second to arrest it. If the two can come to a balance, equilibrium of temperature and current can be attained; if no balance is possible, as will be seen to be the condition on higher voltages, breakdown will take place. This question of the relations between heat development and

dissipation requires quantitative treatment and this will be taken up in the following paragraphs.

HEAT DEVELOPMENT AND DISSIPATION.

The electrical conductivity, C, which is a function of the temperature θ, may be represented by

$$C = C_0 F(\theta),$$

C_0 being conductivity when $\theta = 0$.

The heat developed under any impressed voltage E is thus equal to

$$E^2 C_0 F(\theta).$$

The heat dissipation is a function of θ also, and as a first approximation for small temperature rises, may be taken as proportional to $(\theta - \theta_r)$, θ_r being ambient or "room" temperature.

Thus at equilibrium

$$E^2 C_0 F(\theta) = a(\theta - \theta_r), \qquad (1)$$

and the value of temperature, if any, at which equilibrium is possible can be found by solving this equation for θ. For the present purpose this may most readily be done graphically.

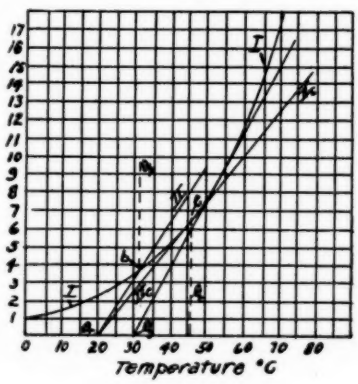

Fig. 2.

Equation (1) may be rewritten

$$F(\theta) = \frac{a}{E^2 C_0}(\theta - \theta_r). \qquad (1a)$$

$F(\theta)$ is a characteristic for the material, and that for boron is plotted in Curve I., Fig. 2. Incidentally, most insulators show a curve concave upward of the general type of the curve here shown.

$\frac{a}{E^2 C_0}(\theta - \theta_r)$ may be plotted also (Curve II., Fig. 2) and is a straight line crossing the θ axis at the value of "room temperature," θ_r. For any ordinary breakdown test the coefficient of heat dissipation "a," the room temperature "θ_r," and the cold conductivity "C_0," are constants and only the applied voltage "E" is varied. Thus under the conditions of experiment, Curve I., Fig. 2, is fixed and the slope of Curve II. is the only quantity which can vary.

It will be seen that for small voltages this slope $a/(E^2 C_0)$ is large and Curve II. intersects Curve I. in a point "b," giving a temperature θ_b, for which there is equilibrium of heat evolution and dissipation. Under

this impressed voltage, therefore, breakdown does not occur, and Curve II. corresponds to the condition of stability met with when the applied voltage is less than the "breakdown" value.

As the value of E, the impressed voltage, is increased the slope of the Curve II. decreases and ultimately a value is reached for which, by reason of the form of Curve I., no intersection of II. with I. occurs. Breakdown therefore takes place under the circuit conditions so represented, as there is no point at which equilibrium of heat generation and dissipation exists. Temperature and current rise thus continue until stopped by the external resistance in the circuit. The reason for the circuit remaining stable indefinitely at lower voltages and becoming unstable after a time at higher voltages, or, in other words, the cause of the "breakdown effect," is thus seen to lie in the effect of internal heating on the variable electrical resistance of the material.

The determination of the precise value of voltage at which stability is changed to instability may, of course, be made from these same curves. It is evident that the limiting voltage dividing breakdown from non-breakdown is that corresponding to the tangent II_c to the Curve I. All higher voltages correspond to lines II. of less slope which cannot intersect Curve I., all lower voltages to lines which do intersect Curve I. and so denote a stable circuit. The tangent thus represents the smallest voltage producing instability and so the "breakdown at infinite time" already referred to.

TEMPERATURE AT BREAKDOWN.

It is obvious that, as Curve I. is characteristic of the material used, the point of tangency of the line II_c starting from a given room temperature θ_r is always the same, for instance, for boron. This temperature, θ_c, is that which would eventually just be reached under the minimum breakdown voltage, *i. e.*, the "breakdown at infinite time," and it is interesting to note that this is always the same for a given material.

It will be seen further that, whenever the specimen has reached a particular value of the temperature, θ, during a test, the heat generated inside it is proportional to the corresponding ordinate of Curve I., while the heat dissipated is proportional to that of Curve II. The difference of these ordinates represents the heat being absorbed by the slab and raising its temperature. Moreover it will be apparent that for voltages not greatly exceeding the "breakdown at infinite time" this difference begins to increase rapidly not long after the temperature θ_c alluded to in the last paragraph is passed. The rapid heat evolution here indicated is what is usually taken as marking "breakdown." As a rough approxi-

mation, "breakdown" may be considered as occurring when the specimen reaches the temperature θ_c. For this reason therefore θ_c may be distinguished as what may be called the "temperature of breakdown," which is of considerable importance and which is furthermore a characteristic of the kind of material under test. Its magnitude is evidently of considerable interest because of its part in determining the occurrence of breakdown. The curves of Fig. 2 show it to be in the vicinity of 45° C. for boron under ordinary test conditions.

TIME REQUIRED TO EFFECT BREAKDOWN.

It has been noted that time is required for any voltage to effect breakdown. Thus it will be seen from the above that this time is that required for that particular voltage to heat the test piece up to the temperature θ_c. It will also be apparent that voltages in excess of the "breakdown at infinite time" heat the specimen up to the necessary temperature with a rapidity determined by such excess and so that the time of breakdown decreases as the impressed voltage increases. The time of breakdown may even be roughly calculated on this basis. The curve of Fig. 3 shows this action as determined experimentally on boron.

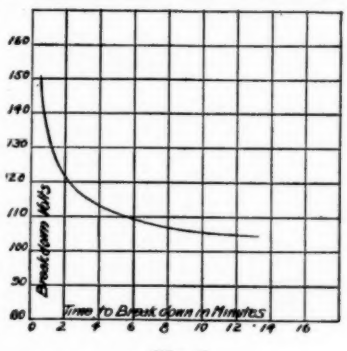

Fig. 3.

EFFECT OF ROOM TEMPERATURE AND THICKNESS.

It is also found that their ambient or "room" temperature greatly affects the voltage at which specimens break down, and this may also be seen from the curves of Fig. 2. Curve I. of course remains unaltered, as it is the characteristic temperature-conductivity curve of the material under test. The straight line II. crosses the temperature axis at a point corresponding to room temperature. Raising the latter from θ_r to θ_s displaces this intersection point to the right as shown. As a result the tangent to Curve I. from this new intercept θ_s has a greater slope than that starting from θ_r. This slope is proportional to the inverse square of the breakdown voltage, so the latter must be smaller as this slope is greater. The breakdown voltage thus decreases with rise of room temperature in accordance with experimental results.

It is also found that the breakdown voltage does not increase proportionally with the thickness of the slab tested, the volts per millimeter being less the thicker the specimen, just as in the breakdown of ordinary

insulations. This can be explained in a general way on the basis of the energy considerations embodied in equations (1) and (1*a*). As explained above, breakdown occurs when the specimen has reached the temperature θ_c, which is a fixed quantity for a given material. Now at that temperature the total heat dissipated from the specimen to its surroundings is proportional to the heat dissipation constant "*a*" of equation (1). But the heat evolved in the slab is certainly not dissipated more readily where part of it has to pass from inside to outside of a thick slab; therefore "*a*" will surely not be greater for thick than for thin slabs. Then the total heat developed in a thick slab cannot be greater than in a thin one, and so the heat evolved per cubic centimeter must be less the thicker the specimen. Now at a given temperature the heat per cubic centimeter is proportional to the square of the voltage gradient; therefore this must decrease as the thickness of the slab increases. The above treatment deals only with rough approximations, but is sufficient to indicate that the voltage gradient at breakdown should be less for thick specimens than for thin ones, as is the case.

CURRENT-TIME CURVES.

In the case of materials so far examined by the writer this temperature θ_c at which breakdown sets in is far below that causing any chemical decomposition in the material. It is possible, therefore, by placing a proper current meter in series with the specimen, to watch the rise of current flowing through the material under any applied voltage during test. As the conductivity is a known function of the temperature, the moment when the breakdown temperature is reached can be determined from the measurement thus given of conductivity. It is possible thus to tell whether break down will take place under any impressed voltage by watching the rate of current rise with time. As an instance of this Fig. 4 gives a curve of current and time during the test of a boron slab at a voltage less than the minimum breakdown. The rate at which current increases with time continually grows less and soon becomes virtually zero. Stability of temperature is attained and breakdown does not take place.

In Fig. 5 is a similar curve on the same specimen at a higher voltage. The slope of the curve first decreases; then after reaching the point marked "*f*" it begins to increase, continuing to grow greater and greater until it becomes practically vertical. Breakdown is taking place; at "*f*" the piece has reached the "breakdown temperature" and breakdown is then inevitable under that voltage of test. The circuit can be interrupted at this point without allowing the action to proceed to destruc-

tively high temperatures. In this way the breakdown voltage may be determined in advance without ever allowing breakdown to occur at all, or the material to be injured by destructively high heating.

BREAKDOWN WITH ALTERNATING VOLTAGES.

The above considerations apply, of course, only to breakdown on tests carried out, as above stated, with direct current. The same general ideas could however be applied to breakdown under alternating voltages except that for the simple "ohmic" resistance losses, the total losses including, for instance, the dielectric hysteresis loss, must be substituted.

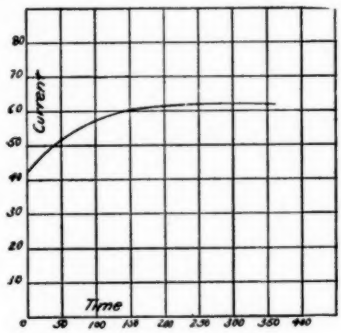

Fig. 4.

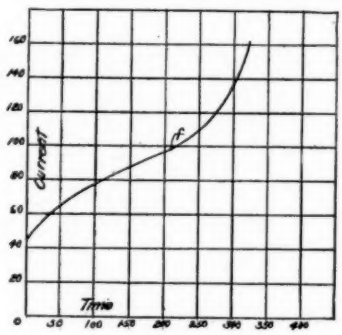

Fig. 5.

It has been found that for a given temperature of the material, in the case of most substances, the losses on A.C. are, just like the D.C. losses, proportional to the square of the applied voltage. Therefore in the equations (1) and (1*a*) given above there may be substituted for the electrical conductivity $C_0F(\theta)$ an analogous quantity, $C_0^1F^1(\theta)$, characteristic of the material under test, and which when multiplied by the square of the applied voltage gives the heat loss. This is the exact parallel of the electrical conductivity on D.C. and, as measurements show it in many cases to be a curve concave upward of the same general type as Curve I., Fig. 2, all the arguments given above as applying to D.C. breakdown should apply equally well to A.C. tests. It is interesting to observe in this connection that the A.C. losses at a given temperature and voltage are in many cases of ordinary insulating materials considerably greater than the D.C. and correspondingly the A.C. breakdown voltage is smaller than the D.C.

It may also be pointed out that in the case of insulations generally an increase of the frequency of the applied voltage increases the dielectric losses, and also the breakdown voltage at higher frequency is less than at low as a rule.

CONCLUSION.

The material boron is thus seen to show under certain voltage stresses many of the characteristic phenomena exhibited by insulators at "breakdown." The existence of a breakdown action, the time needed to effect it, the existence of a critical voltage of "breakdown at infinite time," and the influence thereon of room temperature and thickness of the test specimen are all paralleled by similar characteristics of ordinary insulations. These phenomena in the case of boron are all readily explained by consideration of the variation of its resistance with temperature, as has been shown above. The fact that the same or similar treatment applies to the ordinary insulations points strongly to the possibility that thermal effects are controlling factors in the breakdown of these also.

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A GENERAL THEORY OF ENERGY PARTITION WITH APPLICATIONS TO QUANTUM THEORY.

BY RICHARD C. TOLMAN.

Introduction.—The principle of the equipartition of energy was one of the most definite and important results of the older statistical mechanics, and the contradiction between this principle and actual experimental findings, in particular in the case of the distribution of energy in the hohlraum, has led many physicists to believe that the underlying structure of statistical mechanics must itself be false. More specifically, since statistical mechanics is most conveniently based on the equations of motion in the Hamiltonian form, many critics of the older statistical mechanics have come to the conclusion that Hamilton's equations are themselves incorrect, and indeed some extremists have gone so far as to believe that any set of equations would be incorrect which, like those of Hamilton, take time as a *continuous* variable, since they think that time has in reality an atomic nature and that all changes in configuration take place by jumps.

It is well known, however, as shown by the work of Helmholtz, Maxwell, J. J. Thomson, Planck and others[1] that for all *macroscopic* systems whose behavior is completely known it has been found possible to throw the equations of motion into the Hamiltonian form, provided we make suitable choices for the functional relationships between the generalized coördinates $\phi_1\phi_2\cdots\phi_n$, the generalized velocities $\dot{\phi}_1\dot{\phi}_2\cdots\dot{\phi}_n$,

[1] The appended references may be consulted as an evidence of the general applicability of the principle of least action in all *known* fields of dynamics. The methods of transposing the equations of motion from the form demanded by the principle of least action to the Hamiltonian form are well known. In carrying out this transformation it should be remembered that the system must be taken inclusive enough so as not to be acted on by external forces.

See Helmholtz, (Vorlesungen über theoretische Physik); note the development of electromagnetic theory from a dynamical basis by Maxwell (Treatise on Electricity and Magnetism) and by Larmor (Phil. Trans., *A*-719 (1884), p. 694 (1895)); the treatment of various fields by Sir J. J. Thomson (Applications of Dynamics to Physics and Chemistry, Macmillan, 1888); the presentation of optical theory on a dynamical basis by Maclaurin (The Theory of Light, Cambridge, 1908); and considerable work in newer fields based on the principle of least action by Planck (Ann. d. Physik, *26*, 1 (1908)), Herglotz (Ann. d. Physik, *36*, 493 (1911)), de Wisniewski (Ann. d. Physik, *40*, 668 (1913)), Tolman (Phil. Mag., 28, 583 (1914), and The Theory of the Relativity of Motion, University of California Press, 1917).

the generalized momenta $\psi_1\psi_2\cdots\psi_n$, and the Hamiltonian function H. For this reason the writer is inclined to believe that in the case of the ensembles of *microscopic* systems considered by statistical mechanics it is very unwise to abandon the Hamiltonian equations of motion unless we are absolutely forced to it. It should also be noted that the variables involved in an equation of motion can always be considered as having ultimately a continuous nature, since apparent jumps in configuration can always be accounted for by the assumption of immeasurably high velocities. Such considerations make it necessary to investigate the whole structure of statistical mechanics and determine if the Hamiltonian equations of motion actually do necessitate the principle of the equipartition of energy.

We shall find that the principle of the equipartition of energy is not in the least to be regarded as a necessary consequence of Hamilton's equations, but has been derived from those equations merely because energy has, quite unnecessarily, always been taken as a homogeneous quadratic function of the generalized coördinates. We shall be able, furthermore, to derive a new and very general equipartition law for the equipartition of a function, which reduces to energy for the special case that energy does happen to be a quadratic function of the coördinates. Our methods will further permit us to study the actual partition of energy with various functional relations between energy and the coördinates, and we shall consider a number of interesting systems where energy is not equiparted which have hitherto been neglected. Finally, in the case of the hohlraum, we shall consider a functional relation between energy and the coördinates which does lead to the partition of energy actually found experimentally, and also leads to the absorption and evolution of radiant energy in a relatively discontinuous manner in amounts $h\nu$, thus agreeing with the photoelectric and inverse photoelectric effects.

This treatment of the hohlraum which we shall present leads to the expression

$$\frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$$

for the average energy associated with a mode of vibration of frequency ν, in a hohlraum which has come to thermodynamic equilibrium at temperature T. This expression is known to agree at least substantially with the experimental facts and is the expression proposed by most forms of the so-called quantum theory of radiation. Our treatment of the hohlraum differs, however, from previous forms of quantum theory in not disturbing

in the least the fundamental structure of the familiar classical statistical mechanics. In essence, our development adopts the essentials of the older statistical mechanics, and merely grafts on to it the new idea, that energy is not necessarily a quadratic function of the generalized coördinates and momenta which appear in the equations of motion in the Hamiltonian form.[1] The methods of attack, which are here considered, are moreover much more general than any hitherto employed by the quantum theory, since they permit a study of the partition of energy for an infinite variety of forms of relation between energy and the coordinates. Thus in the present article, we shall consider the energy partition in a number of systems besides those which can be treated by the quantum theory, including for example the partition of energy in a gas subjected to the action of gravity. Indeed it is to be specially emphasized that we shall find the structure of statistical mechanics quite big enough to account for any desired number of different modes of energy distribution besides the particular one proposed by the quantum theory.[2]

PART I. STATISTICAL MECHANICS.

The Equations of Motion.—Consider an isolated system whose state is defined by the n generalized coördinates $(\phi_1\phi_2\cdots\phi_n)$ and the corresponding momenta $(\psi_1\psi_2\cdots\psi_n)$. Then in accordance with Hamilton's equations we may write the equations of motion for this system in the form

$$\begin{aligned} \frac{\partial H}{\partial \phi_1} &= -\dot{\psi}_1, \quad \frac{\partial H}{\partial \phi_2} = -\dot{\psi}_2, \quad \cdots, \\ \frac{\partial H}{\partial \psi_1} &= \dot{\phi}_1, \quad \frac{\partial H}{\partial \psi_2} = \dot{\phi}_2, \quad \cdots, \end{aligned} \tag{1}$$

where H is the Hamiltonian function, and $\dot{\psi}_1 = (d\psi_1/dt)$, etc.

Geometrical Representation.—Employing the methods so successfully used by Jeans,[3] we may now think of the state of the system at any instant as determined by the position of a point plotted in a $2n$-dimensional space. Suppose now we have a large number of systems of the same structure but differing in state, then for each system we should have at each instant a corresponding point in our $2n$-dimensional space, and as the systems change in state, in accordance with equations (1), the points will describe stream lines in the generalized space.

[1] The investigations already referred to show the possibility of a variety of functional relationships between energy and the generalized coördinates and momenta.

[2] This fact might assume unexpected importance if more accurate measurements of the distribution of energy in the hohlraum should lead us to discard Planck's formula as experimentally correct.

[3] The Dynamical Theory of Gases, 2d edition, Cambridge, 1916.

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The Maintenance of Uniform Density.—Suppose now that the points were originally distributed uniformly throughout the space, then it is a necessary consequence of our equations of motion that the distribution will remain uniform. To show this, we note that we may write for the rate at which the density at any point is increasing:

$$\frac{d\rho}{dt} = -\rho\left(\frac{\partial\dot{\phi}_1}{\partial\phi_1}+\frac{\partial\dot{\phi}_2}{\partial\phi_2}+\frac{\partial\dot{\phi}_3}{\partial\phi_3}+\cdots+\frac{\partial\dot{\psi}_1}{\partial\psi_1}+\frac{\partial\dot{\psi}_2}{\partial\psi_2}+\frac{\partial\dot{\psi}_3}{\partial\psi_3}+\cdots\right),$$

and since our equations of motion (1) evidently lead to the relations

$$\frac{\partial\dot{\phi}_1}{\partial\phi_1}+\frac{\partial\dot{\psi}_1}{\partial\psi_1}=0,$$

$$\frac{\partial\dot{\phi}_2}{\partial\phi_2}+\frac{\partial\dot{\psi}_2}{\partial\psi_2}=0, \text{ etc.},$$

we see that the original uniform density will not change.

This important result means that there is no tendency for the representative points to crowd into any particular part of the generalized space, and hence if we start some one system going and plot its state in our generalized space, we may assume,[1] that, after an indefinite lapse of time, its representative point is equally likely to be in any one of the infinitesimal elements of equal volume ($d\phi_1 d\phi_2 d\phi_3 \cdots d\psi_1 d\psi_2 d\psi_3 \cdots$) into which we can divide our generalized space, provided of course the coordinates for the location of this element correspond to the actual energy content of our system.

Microscopic State.—As a convenient nomenclature, we shall say that a statement of the particular element of volume ($d\phi_1 d\phi_2 d\phi_3 \cdots d\psi_1 d\psi_2 d\psi_3 \cdots$) in which the representative point for our given system is found is a specification of the *microscopic state of the system. And the principle, which we have just obtained, states that all the different microscopic states possible have the same probability.*

Statistical State.—Let us suppose now that our system is a thermodynamic one composed of a large number of identical elements, such as atoms, molecules, oscillators, modes of vibration, etc. We may let N_A, N_B, N_C, etc., be the number of elements of each of the different kinds A, B, C, etc., which go to make up the complete system, and may consider our original $2n$ coördinates and momenta as divided up among these different elements.

For such a thermodynamic system we shall be particularly interested in the number of elements of any particular kind A which have coordinates and momenta falling in a given infinitesimal range ($d_A\phi_1\, d_A\phi_2$

[1] It is not within the scope of our present undertaking to enter into the vexed discussions as to the validity of this assumption.

$\cdots d_A\psi_1\, d_A\psi_2 \cdots$) and this determines what we shall call the *statistical state of the system.*

The microscopic state of the system and the statistical state differ in that the former determines the coördinates and momenta for each individual element, while the latter only states the number of elements of the different kinds which have coördinates and momenta of a given magnitude, without making any distinction as to which particular elements are taken to supply a quota. Thus we see that, corresponding to a given statistical state of the system, there will be a large number of microscopic states, and, since we have already seen that all microscopic states are equally probable, we obtain the important conclusion that the probability of occurrence for a given statistical state is proportional to the number of microscopic states to which it corresponds.

Probability of a Given Statistical State.—Let us now specify a given statistical state by stating that ${}_1N_A\ {}_2N_A\ {}_3N_A \cdots {}_1N_B\ {}_2N_B\ {}_3N_B \cdots {}_1N_C\ {}_2N_C\ {}_3N_C \cdots$, etc., are the number of elements of each of the kinds, which have values of coördinates and momenta which fall in the particular infinitesimal ranges Nos. $1A$, $2A$, $3A$, $\cdots$, $1B$, $2B$, $3B$, $\cdots$, etc. Then it is evident from the principles of permutation that the number of microscopic states corresponding to this statistical state will be:

$$W = \frac{\lfloor N_A \lfloor N_B \lfloor N_C \cdots}{\lfloor {}_1N_A \lfloor {}_2N_A \lfloor {}_3N_A \cdots \lfloor {}_1N_B \lfloor {}_2N_B \cdots \lfloor {}_3N_B \lfloor {}_1N_C \lfloor {}_2N_C \lfloor {}_3N_C \cdots} \tag{2}$$

and we shall call this the *probability* of the given statistical state, without bothering to introduce any proportionality factor.

Let us assume now that each of the numbers ${}_1N_A\ {}_2N_B$, etc., are large enough so that we may apply the Stirling Formula,

$$\lfloor N = \sqrt{2\pi N}\left(\frac{N}{e}\right)^N. \tag{3}$$

Introducing into (2), taking the logarithm of W for greater convenience, and omitting negligible terms we obtain:

$$\begin{aligned}
\log W = &- N_A\left(\frac{{}_1N_A}{N_A}\log\frac{{}_1N_A}{N_A} + \frac{{}_2N_A}{N_A}\log\frac{{}_2N_A}{N_A} + \frac{{}_3N_A}{N_A}\log\frac{{}_3N_A}{N_A} + \cdots\right) \\
&- N_B\left(\frac{{}_1N_B}{N_B}\log\frac{{}_1N_B}{N_B} + \frac{{}_2N_B}{N_B}\log\frac{{}_2N_B}{N_B} + \frac{{}_3N_B}{N_B}\log\frac{{}_3N_B}{N_B} + \cdots\right) \\
&- N_C\left(\frac{{}_1N_C}{N_C}\log\frac{{}_1N_C}{N_C} + \frac{{}_2N_C}{N_C}\log\frac{{}_2N_C}{N_C} + \frac{{}_3N_C}{N_C}\log\frac{{}_3N_C}{N_C} + \cdots\right) \\
&- \text{etc.}
\end{aligned} \tag{4}$$

The ratios ${}_1N_A/N_A$, ${}_2N_A/N_A$, etc., evidently give the probability that

any particular element of the kind in question shall have values of the coördinates and momenta falling within particular infinitesimal ranges ($d_A\phi_1\, d_A\phi_2 \cdots d_A\psi_1\, d_A\psi_2 \cdots$) Nos. 1 A, 2 A, etc., provided the system is in the given statistical state. Let us denote these ratios by the symbols ${}_1w_A$, ${}_2w_A$, etc.,

$$ {}_iw_A = \frac{{}_iN_A}{N_A}, \quad {}_iw_B = \frac{{}_iN_B}{N_B}, \quad {}_iw_C = \frac{{}_iN_C}{N_C}, \quad \text{etc.} \tag{5} $$

Then we may rewrite equation (4) in the form

$$ \log W = -N_A \sum_{i=1,2,3,\ldots} {}_iw_A \log {}_iw_A - N_B \sum_{i=1,2,3,\ldots} {}_iw_B \log {}_iw_B - N_C \sum_{i=1,2,3,\ldots} {}_iw_C \log {}_iw_C - \cdots. \tag{6} $$

State of Maximum Probability.—Having obtained this expression for the probability of a given statistical state, let us determine what particular state is the most probable with a given energy content. The condition of maximum probability will evidently be:

$$ \delta \log W = -N_A \Sigma(\log {}_iw_A + 1)\delta\, {}_iw_A - N_B \Sigma(\log {}_iw_B + 1)\delta\, w_B \cdots = 0. \tag{7} $$

The variation δ, however, cannot be carried out entirely arbitrarily since the number of elements of any particular kind cannot be varied and the total amount of energy is to be a constant.

In accordance with equations (5) we may write

$$ N_A = N_A \Sigma\, {}_iw_A, \quad N_B = N_B \Sigma\, {}_iw_B, \quad \text{etc.}, $$

and since the total number of elements N_A, N_B, etc., of each kind cannot be varied we have

$$ N_A \Sigma\, \delta\, {}_iw_A = 0, \quad N_B \Sigma\, \delta\, {}_iw_B = 0, \quad \text{etc.} \tag{8} $$

Furthermore, let us write the total energy of the system equal to the sum of the energies of the individual elements,

$$ E = N_A \Sigma\, {}_iw_A\, {}_iE_A + N_B \Sigma\, {}_iw_B\, {}_iE_B + \cdots, $$

where ${}_iE_A$, etc., is the energy of an element of kind A with values of coördinates and momenta falling in the infinitesimal region No. iA, etc. Since E is to remain constant during the variation we may write

$$ \delta E = N_A \Sigma\, {}_iE_A \delta w_A + N_B \Sigma\, {}_iE_B \delta w_B + \cdots = 0. \tag{9} $$

The simultaneous equations (7) (8) and (9) may now be solved by the familiar method of undertermined multipliers giving us

$$ \begin{aligned} &\log {}_iw_A + 1 + \lambda\, {}_iE_A + \mu_A = 0, \quad i = 1\,2\,3\cdots, \\ &\log {}_iw_B + 1 + \lambda\, {}_iE_B + \mu_B = 0, \quad i = 1\,2\,3\cdots, \end{aligned} \tag{10} $$

etc.

The quantities λ, μ_A, μ_B, etc., are undetermined multipliers, where it should be specially noticed that λ is the same quantity for all the equations, while μ_A, μ_B, etc., depend on the particular kind of element in question.

For our purposes these equations can be more conveniently written in the form

$$\begin{aligned} {}_iw_A &= \alpha_A e^{-\beta\, {}_iE_A}, \\ {}_iw_B &= \alpha_B e^{-\beta\, {}_iE_A}, \\ &\text{etc.}, \end{aligned} \tag{11}$$

where e is the base of the natural system of logarithms and the constants α_A, α_B, etc., correspond to the earlier μ_A, μ_B, etc., and β corresponds to μ. These are the desired equations which describe the state of maximum probability. Thus, in accordance with the equations of definition (5), ${}_iw_A$ is the probability that any particular element kind A will have values of coördinates and momenta falling in the particular infinitesimal region, $(d_A\phi_1, d_A\phi_2, \cdots, d_A\psi_1, d_A\psi_2, \cdots)$, No. iA, when the system has attained the state of maximum probability.

Introduction of a Continuous Variable.—The quantity ${}_iw_A$ determines the number of elements that fall in the specific region No. iA. We have seen, however, in equations (11) that ${}_iw_A$ is determined by the energy corresponding to this region, and this in turn is a function of the coördinates and momenta. This makes it possible to introduce a new and convenient quantity, a variable, w_A, which is a function of these coördinates and momenta, and which gives the probability, *per unit generalized volume*, that a given element of kind A will have coördinates and momenta corresponding to the energy E_A, we may then write

$$\begin{aligned} w_A d_A\phi_1 d_A\phi_2 \cdots d_A\psi_1 d_A\psi_2 \cdots &= a_A e^{-\beta E_A} d_A\phi_1 d_A\phi_2 \cdots d_A\psi_1 d_A\psi_2 \cdots, \\ w_B d_B\phi_1 d_B\phi_2 \cdots d_B\psi_1 d_B\psi_2 \cdots &= a_B e^{-\beta E_B} d_B\phi_1 d_B\phi_2 \cdots d_B\psi_1 d_B\psi_2 \cdots, \end{aligned} \tag{12}$$

as expressions for the chance that a particular element of kind A, B, etc., will have values for coördinates and momenta falling in the infinitesimal ranges indicated.

Final Expression for the Distribution of Elements in State of Maximum Probability.—It will be noticed that the constants a_A, a_B, etc., which occur in equations (12) correspond to the μ_A, μ_B, etc., in equations (10) and hence these values will be determined by the particular kind of element A, B, etc., involved. β, on the other hand, corresponds to the earlier λ and hence its value is independent of the particular kind of element involved. In case the elements involved are the molecules of a perfect monatomic gas, it is well known that β has the value of $1/kT$,

where k is the ordinary gas constant divided by Avagadro's number, and T is the absolute temperature. Hence we may now write as our final expression for the probability that a given element of any particular kind will have values of coördinates and momenta falling within a given infinitesimal range,

$$ae^{-E/kT}d\phi_1 d\phi_2 \cdots d\psi_1 d\psi_2 \cdots, \tag{13}$$

where the value of a depends on the particular kind of element A, B, C, etc., in which we are interested, and E is the energy of one of the elements, expressed as a function of its generalized coördinates and momenta $(\phi_1\phi_2\cdots\psi_1\psi_2\cdots)$.

Two Fundamental Equations of Statistical Mechanics.—Since any element must have *some* value for its coördinates and momenta we may write the important equation,

$$\int_{\infty}\int_{\infty}\cdots\int_{\infty}\int_{\infty}\cdots ae^{-E/kT}d\phi_1 d\phi_2\cdots d\psi_1 d\psi_2\cdots = 1, \tag{14}$$

where the limits of the integration are such as to include all possible values of the ϕ's and ψ's.

Furthermore, it is evident that we may write for the average value of any property P of an element, the equation

$$P_{av} = \int_{\infty}\int_{\infty}\cdots\int_{\infty}\int_{\infty}\cdots ae^{-E/kT}Pd\phi_1 d\phi_2\cdots d\psi_1 d\psi_2\cdots, \tag{15}$$

where P is to be taken as a function of the coördinates and momenta, and the limit of integration is as above.

The General Equipartition Law.—We may now derive a very general equipartition law. Let us integrate the left-hand side of equation (14) by parts with respect to ϕ_1, we obtain

$$\left[\int\cdots\int\int\cdots ae^{-E/kT}\phi_1 d\phi_2\cdots d\psi_1 d\psi_2\cdots\right]_{\phi_1 = \text{lower limit}}^{\phi_1 = \text{upper limit}} - \int\int\cdots\int\int\cdots ae^{-E/kT}\phi_1\left(\frac{-1}{kT}\right)\frac{\partial E}{\partial\phi_1}d\phi_1 d\phi_2\cdots d\psi_1 d\psi_2\cdots = 1. \tag{16}$$

Let us confine ourselves now to cases in which ϕ_1 becomes either zero or infinity at the two limits, and in which E becomes infinite if ϕ_1 does. Then the first term of (16) vanishes and we may write

$$\int\int\cdots\int\int\cdots ae^{-E/kT}\phi_1\frac{\partial E}{\partial\phi_1}d\phi_1 d\phi_2\cdots d\psi_1 d\psi_2\cdots = kT. \tag{17}$$

In accordance with (15), however, this gives us the average value of $[\phi_1(\partial E/\partial\phi_1)]$ and hence, applying similar consideration to the other coördinates and momenta, we may now write as our general equipartition law:

$$\left[\phi_1 \frac{\partial E}{\partial \phi_1}\right]_{av} = \left[\phi_2 \frac{\partial E}{\partial \phi_2}\right]_{av} \cdots = \left[\psi_1 \frac{\partial E}{\partial \psi_1}\right]_{av} = \left[\psi_2 \frac{\partial E}{\partial \psi_2}\right]_{av} = \cdots = kT, \quad (18)$$

and this law will apply in all cases in which the above condition as to the limits of integration is fulfilled.

The General Equation for the Partition of Energy.—In the particular case that the energy is a homogeneous quadratic function of the coördinates and momenta the above equation (18) will evidently reduce to the value $\frac{1}{2}kT$ for the energy associated with each coördinate or momentum, which is the familiar principle of the equipartition of energy.

Whatever may be the relation, however, between energy and the coördinates and momenta, we may obtain its average value for a given kind of element with the help of equation (15), which permits us to write

$$E_{av} = \int\int \cdots \int\int \cdots a e^{-E/kT} E d\phi_1 d\phi_2 \cdots d\psi_1 d\psi_2 \cdots. \quad (19)$$

In order to eliminate the constant a we may divide (19) by (14) and obtain,

$$E_{av} = \frac{\int\int \cdots \int\int \cdots e^{-E/kT} E d\phi_1 d\phi_2 \cdots d\psi_1 d\psi_2 \cdots}{\int\int \cdots \int\int \cdots e^{-E/kT} d\phi_1 d\phi_2 \cdots d\psi_1 d\psi_2 \cdots}. \quad (19a)$$

We may now apply equations (18) and (19*a*) to obtain information as to the partition of energy in a number of interesting cases.[1]

PART II. MISCELLANEOUS APPLICATIONS.

Gas Subjected to Gravity.—For the first application of our equations let us consider a monatomic gas subjected to the action at gravity, *in a tube of infinite length.* Considering the Z axis as vertical we can write for the energy of any given molecule,

$$E = mgz + \frac{m\dot{x}^2}{2} + \frac{m\dot{y}^2}{2} + \frac{m\dot{z}^2}{2},$$

where z is the height of the molecule above the surface of the earth. In terms of the components of momentum, our expression for energy may be rewritten:

$$E = mgz + \frac{1}{2m}\psi_x^2 + \frac{1}{2m}\psi_y^2 + \frac{1}{2m}\psi_z^2,$$

[1] In applying these equations it is to be noticed that we do not need to make the elements into which we divide our statistical system agree with what are ordinarily thought of as the physical elements of the system. Thus if our system is a quantity of a monatomic gas, instead of taking each atom with its three positional coördinates and its three momenta as an element we may take these variables as belonging to six different elements. Indeed it is obvious, from our methods of deduction, that we shall need to class coördinates and momenta together as belonging to the same element only in groups large enough so that any given coördinate momentum will not appear in the expression for the energy of more than one of our elements.

where the components of momentum are given by the equations

$$\psi_x = m\dot{x}, \quad \psi_y = m\dot{y}, \quad \psi_z = m\dot{z}.$$

Applying our equipartition equation (18) we obtain

$$[mgz]_{av} = \left[\frac{1}{m}\psi_x^2\right]_{av} = \left[\frac{1}{m}\psi_y^2\right]_{av} = \left[\frac{1}{m}\psi_z^2\right]_{av} = kT,$$

or, introducing the equations defining momenta, we obtain

$$[mgz]_{av} = kT, \quad \left[\frac{m\dot{x}^2}{2}\right]_{av} = \left[\frac{m\dot{y}^2}{2}\right]_{av} = \left[\frac{m\dot{z}^2}{2}\right]_{av} = \tfrac{1}{2}kT.$$

And we see that according to our equipartition law, the average potential energy per molecule is *twice* as great as the average kinetic energy in any direction.

This is a particularly simple case of a deviation from the principle of the equipartition of energy, and of course it could have been shown by methods which have long been familiar, that the average potential energy per molecule is twice as great as the average component of kinetic energy. It should be specially noticed that this is a deviation from the principle of the equipartition of energy which bears no relation to those which have more recently been discovered and studied by the quantum theory.

The Energy Any Simple Power of the Coördinates.—The above deviation from the equipartition of energy was due to the fact that the potential energy of these molecules was proportional to the first power instead of to the square of the coördinate involved. We may point out with the help of equation (18) what the general relation will be. If the energy for a given elementary coördinate or momentum is proportional to the nth power of that invariable,

$$E = c\phi^n, \tag{20}$$

then by (18) we shall have

$$E_{av} = \frac{kT}{n}.$$

Thus, for example, if we had in our system oscillating elements in which the restoring force, instead of following Hook's law, was proportional to the square of the displacement, then the average potential energy of these oscillators would be $\frac{1}{3}kT$ instead of the familiar $\frac{1}{2}kT$.

These considerations will be of value in case we find it convenient to express the energy of an element by an empirical formula of the form

$$E = a + b\phi + c\phi^2 + d\phi^3 + \cdots.$$

Relativity Mechanics.—As another example of a deviation from the

principle of the equipartition of energy, we may consider a monatomic gas whose molecules are considered as particles, obeying the new "relativity" laws of motion instead of Newton's laws of motion, which we now know are only the approximate form assumed by the correct laws of motion at low velocities.

According to these new laws of motion we must write for the components of momentum of a particle:

$$\psi_x = \frac{m_0\dot{x}}{\sqrt{1 - \frac{\dot{x}^2 + \dot{y}^2 + \dot{z}^2}{c^2}}},$$

$$\psi_y = \frac{m_0\dot{y}}{\sqrt{1 - \frac{\dot{x}^2 + \dot{y}^2 + \dot{z}^2}{c^2}}}, \tag{21}$$

$$\psi_z = \frac{m_0\dot{z}}{\sqrt{1 - \frac{\dot{x}^2 + \dot{y}^2 + \dot{z}^2}{c^2}}},$$

where m_0 is the mass of the particle at rest and c is the velocity of light.

For the kinetic energy of the particle we may write

$$E = \frac{m_0c^2}{\sqrt{1 - \frac{\dot{x}^2 + \dot{y}^2 + \dot{z}^2}{c^2}}}, \tag{22}$$

a quantity which except for a constant reduces to $\frac{1}{2}m_0(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)$ at low velocities. In terms of the momenta we may rewrite this expression for the kinetic energy in the form

$$E = c\sqrt{c^2m_0^2 + \psi_x^2 + \psi_y^2 + \psi_z^2}. \tag{23}$$

Applying equation (18) we obtain

$$\left[\psi_x \frac{c\psi_x}{\sqrt{c^2m_0^2 + \psi_x^2 + \psi_y^2 + \psi_z^2}}\right]_{av} = \left[\psi_y \frac{c\psi_y}{\sqrt{c^2m_0^2 + \psi_x^2 + \psi_y^2 + \psi_z^2}}\right]_{av}$$
$$= \text{etc.} = kT,$$

and introducing our previous equations, this may be written

$$\frac{1}{2}\left[\frac{m_0\dot{x}^2}{\sqrt{1 - \frac{\dot{x}^2 + \dot{y}^2 + \dot{z}^2}{c^2}}}\right]_{av} = \frac{1}{2}\left[\frac{m_0\dot{y}^2}{\sqrt{1 - \frac{\dot{x}^2 + \dot{y}^2 + \dot{z}^2}{c^2}}}\right]_{av}$$
$$= \frac{1}{2}\left[\frac{m_0\dot{z}^2}{\sqrt{1 - \frac{\dot{x}^2 + \dot{y}^2 + \dot{z}^2}{c^2}}}\right]_{av} = \tfrac{1}{2}kT. \tag{24}$$

We thus see that in relativity mechanics we have the equipartition of a function which reduces to the kinetic energy $\frac{1}{2}m_0\dot{x}^2$, etc., at low velocities, but at high velocities is not even the same as the *relativity* expression for energy.[1]

These few examples are sufficient to illustrate the application of our methods, in fields other than those treated by the quantum theory. Let us now turn our attention to the partition of energy between the different modes of vibration of a hohlraum.

PART III. APPLICATION TO THE HOHLRAUM.

The Idea of Quanta.—In developing a theory of the hohlraum, we may base our considerations on the fact that radiant energy is known to be absorbed and evolved substantially in quanta of the amount $h\nu$, where h is Planck's new constant and ν is the frequency of the radiation involved. This is an experimental fact, illustrated most simply by the photo-electric effect and the inverse photo-electric effect, and is certainly the expression of a fundamental characteristic of radiant energy.

This important fact can be incorporated in our new system of statistical mechanics by assuming that the energy associated with a given mode of vibration in the hohlraum increases with the amplitude of the vibrations in a relatively discontinuous fashion by amounts of the magnitude $h\nu$. If ϕ is a generalized coördinate which determines the displacement for a given mode of vibration and ψ is the corresponding generalized momentum, then in the older dynamics the energy associated with the mode would have been given by the formula

$$E = k\phi^2 + l\psi^2, \tag{25}$$

where k and l are constants. According to this formula the potential energy $k\phi^2$ increases continuously with the square of the displacement and the kinetic energy $l\psi^2$ with the square of the momentum.

In our new dynamics let us assume that the energy is practically zero until $k\phi^2 + l\psi^2$ reaches the value $h\nu$ and that it then increases with great suddenness to the value $h\nu$, remaining again practically constant until it increases to the amount $2h\nu$, when $k\phi^2 + l\psi^2$ itself reaches the value $2h\nu$, and so on, for following intervals, the energy attaining successively the values $3h\nu$, $4h\nu$, etc.

Expression for Energy.—Such a relation between energy and the coordinates can be expressed algebraically by the equation

$$E = h\nu\{e^{-[h\nu/(k\phi^2+l\psi^2)]^n} + e^{-[2h\nu/(k\phi^2+l\psi^2)]^n} + e^{-[3h\nu/(k\phi^2+l\psi^2)]^n} + \cdots\}, \tag{26}$$

[1] This new equipartition law for the special case of relativity mechanics was first derived by the author, Phil. Mag., *28*, 583 (1914). The same article or an earlier one by Jüttner, Ann. d. Physik, *34*, 856 (1911), may be consulted for an investigation of the actual energy partition in this case.

where n is some number large enough so that the exponents of e change suddenly from minus infinity to zero when $k\phi^2 + l\psi^2$ assumes the successive values $h\nu$, $2h\nu$, $3h\nu$, etc. If n were itself given the value infinity, the energy would increase in absolutely abrupt steps of the magnitude $h\nu$. It is not our belief, however, that the energy changes absolutely abruptly at the points in question, since if this were the case the whole application of our statistical mechanics would be fallacious, since it is based on the Hamiltonian equations which presuppose a motion which is at least continuous when regarded from a fine-grained enough point of view. Furthermore it is not to be supposed that the *precise* relation between energy and the coördinates is necessarily given by equation (26). The expression presented or any other which makes the energy increase in the way described, substantially in quanta, is quite suitable for the purposes of integration which we have in view, but might not be suitable, if we should desire to differentiate (26) for the purpose of determining the equations of motion in the Hamiltonian form.

Before leaving the discussion of equation (26), we should point out that ν is the frequency of the particular mode of vibration involved and h is Planck's new universal constant which has the magnitude 12.83×10^{-27} erg $\times$ seconds, so that even with a frequency of many billions per second, the energy would apparently increase with the amplitude of vibration in a perfectly continuous fashion in accordance with the simple equation $E = k\phi^2 + l\psi^2$, which has been made familiar by experimentation with those everyday vibrating systems whose frequencies are low.

Partition of Energy in the Hohlraum.—Having described the relation between energy and the coördinates which we believe to exist, let us proceed to determine the partition of energy in the hohlraum, by the methods which we have developed in the earlier part of the article. In accordance with equation (19*a*) we may write for the average energy associated with a given mode of vibration,

$$E_{av} = \frac{\int\int e^{-E/kT} E d\phi d\psi}{\int\int e^{-E/kT} d\phi d\psi}.$$

In order to evaluate these integrals for our particular case, we may note in accordance with equation (26), that the energy E will have the value zero for all values of ϕ and ψ which lie inside the ellipse $k\phi^2 + l\psi^2 = h\nu$, the value $h\nu$ for all values of ϕ and ψ falling in the space between this ellipse and the concentric one $k\phi^2 + l\psi^2 = 2h\nu$, and so on for successive concentric ellipses. This permits us to rewrite the above equation in the form

$$E_{av} = \frac{\iint\limits_{0<k\phi^2+l\psi^2<h\nu} e^{0} d\phi d\psi + \iint\limits_{h\nu<k\phi^2+l\psi^2<2h\nu} e^{-h\nu/kT} h\nu d\phi d\psi + \iint\limits_{2h\nu<k\phi^2+l\psi^2<3h\nu} e^{-2h\nu/kT} 2h\nu d\phi d\psi + \cdots}{\iint\limits_{0<k\phi^2+l\psi^2<h\nu} e^{0} d\phi d\psi + \iint\limits_{h\nu<k\phi^2+l\psi^2<2h\nu} e^{-h\nu/kT} d\phi d\psi + \iint\limits_{2h\nu<k\phi^2+l\psi^2<3h\nu} e^{-2h\nu/kT} d\phi d\psi + \cdots}.$$

Since the area enclosed by the successive ellipses increases by equal steps of the amount $(\pi h\nu/\sqrt{kl})$, the above expression can be reduced to

$$E_{av} = \frac{h\nu(e^{-h\nu/kT} + 2e^{-2h\nu/kT} + 3e^{-3h\nu/kT} + \cdots)}{1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + e^{-3h\nu/kT} \cdots)},$$

which upon division is seen to be

$$E_{av} = \frac{h\nu}{e^{h\nu/kT} - 1}, \tag{27}$$

which is the well-known expression, assumed by the quantum theory upon *empirical* grounds, as the average energy for a mode of vibration of frequency ν. The result is of significance in showing that our generalized dynamics, in which the energy can be any function of the coördinates and momenta, leads to a statistical mechanics broad enough to account for the actual partition of energy found in the hohlraum.

Emission of Energy by Quanta.—Before leaving this discussion we should point out that the relation (26) between energy and the generalized coördinates which we have chosen, not only accounts, as we have just seen, for the partition of energy in the hohlraum, but also explains the photo-electric and the inverse photo-electric effects. This arises from the fact that in accordance with the fundamental structure of our system of statistical mechanics all microscopic states for a given mode of vibration are equally probable, and since the vast majority of these microscopic states correspond to an energy content, which is an exact multiple of $h\nu$, we shall expect generally to find radiant energy absorbed and emitted in amounts $h\nu$ or some multiple thereof.

Nature of the Electromagnetic Field.—It is, further, to be pointed out, if we are permitted to trespass for a moment in a field of uncertain speculation, that our relation (26) between energy and the coördinates indicates a somewhat fibrous structure for the electromagnetic field when viewed from a fine-grained enough, and not *too* fine-grained, point of view. It seems to the writer, that this conclusion might furnish support to those theories of the atom[1] which assign very definite positions,

[1] See, for example, Lewis, J. Amer. Chem. Soc., *38*, 762 (1916).

with reference to the positive nucleus, to those electrons which determine the chemical properties of the atom, since the fibrous structure of the electromagnetic field surrounding the positive nucleus might easily provide rather definite pockets where these electrons would find their positions of equilibrium.

PHOTOELECTRIC EFFECTS ON MERCURY DROPLETS.

BY JOHN B. DERIEUX.

SIMULTANEOUS DISCHARGES.

IT has been shown by Professor R. A. Millikan and Mr. Harvey Fletcher that never more than one elementary charge at a time is detached from a neutral air molecule by primary or secondary X-rays.[1]

The question naturally arises as to whether in photoelectric effect more than one electron at a time is detached from a molecule of the metal by the ultra-violet light. Particles suspended in a Millikan condenser furnish a convenient manner of making this determination.

A. Joffe in work in the photoelectric effect on small particles by the above-mentioned method notes variations in the time of liberation with the size of the particle, intensity of illumination, and wave-length of the light.[2] He made no study, however, of whether more than one electron at a time was liberated, but his tables show doubles in a few instances. Edgar Myer and Walther Gerlach, by the same method, determined the variation in the time of liberation with pressure of the surrounding air, but neither do they take note as to simultaneous liberations.[3]

METHOD.

Mercury droplets were secured as in the work on the elementary charge and by the method used there the number of units of charge on them was determined. Ultra-violet light was allowed to fall upon them until a change in their charge was noticed. The new number of units of charge was then determined and the difference between the two taken as the number of units of the change in charge.

APPARATUS.

The electric condenser for the apparatus was composed of two circular plates about 15 cm. in diameter separated about 1.8 cm. and supported in a horizontal position. The potentials of the condenser were obtained from a 5,000-volt battery of storage cells. A variation in the potential

[1] Phil. Mag., June, 1911.

[2] Sitzungsberichte d. Bayer Akad., 1913.

[3] Arch. des Sci. and Nat., March, 1914.

was secured by means of a controller consisting of a revolving handle and contact points connected to different points in the battery. A quartz mercury-vapor lamp was used as a source for the ultra-violet light, an X-ray tube for the ionization of the air, and a right carbon arc for the illumination of the droplets. A cathetometer telescope with a scale in the eyepiece was used in observing.[1]

MANIPULATION.

The mercury lamp was placed in the plane passing midway between the condenser plates and at an average distance of about 50 cm. from their centers. The light from it entered through a diaphragm which was so adjusted that the beam in the condenser had a height of about 1 cm. and passed through without striking the plates. Admission was controlled by a shutter just in front of the diaphragm.

With the shutter closed, a droplet was secured and a small negative charge given it, through ionization by the X-rays. The times required for it to fall 1 millimeter under gravity and to rise 1 millimeter under the full potential of the battery were noted. The assistant then connected the first point of the controller to the battery at such a place that the potential obtained from it was sufficient to hold the drop suspended or cause it to slowly rise. The droplet was then placed about midway between the plates so that it would be in the path of the ultra-violet beam and the shutter was opened until an electron had been liberated. With the droplet balanced, as indicated, the instant of liberation was very marked, for the droplet which had previously been stationary, or gradually rising, suddenly began to descend. The rising speed under the full potential of the battery was then taken, a balance secured from the second point of the controller and another exposure made. This process was continued until the droplet was discharged or the full potential of the batteries was required to produce a balance. The droplet was then recharged through ionization by the X-rays and another series taken. With the points of the controller connected as in the first series, a balance of the droplet in any case could be secured by simply moving the controller handle to the proper point. It was of course necessary to reconnect the controller for the initial series on each droplet.

Assuming electricity to be atomic in structure and the unit of charge to be 4.77×10^{-10} e.s.u. it was sufficiently accurate to take readings over a distance of only 1 millimeter with a stop watch in order to deter-

[1] The apparatus and arrangement was the same as that used in work by the author on "Use of Mercury Droplets in Millikan's Experiment," a detailed drawing and description of which was published in The PHYSICAL REVIEW for March, 1918.

mine, without a doubt, the number of changes on a droplet. The computations were made as in the work on the elementary charge.

RESULTS.

In Tables I., II., III., and IV. are shown sets of typical observations. The numbers in the columns headed t_g indicate the time in seconds required for the droplet to fall 1 millimeter under gravity, those under t_F,

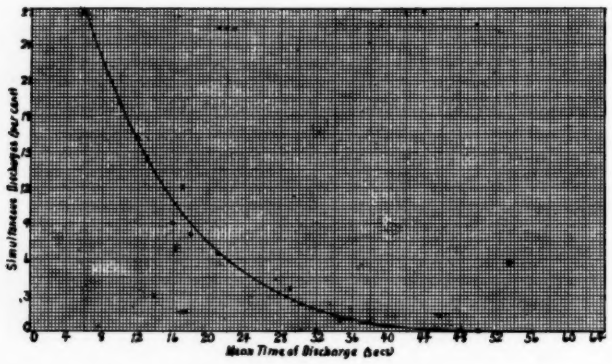

Fig. 1.

the time in seconds under field. Table V. gives the results for all the droplets observed. In the column headed a are recorded the radii of the droplets.

DISCUSSION OF RESULTS ON SIMULTANEOUS DISCHARGES.

As is shown in Table V., simultaneous discharges occurred in several instances, but it may be noticed that the percentage of them decreased with an increase in the mean time of liberation, becoming zero, as is strikingly shown by the graph, at a value of about 50 seconds.

A plausible explanation of this is found in the wide extremes of the times of liberation. It is possible, and even probable, that if a minimum of .5 of a second occurred on a droplet having a maximum of 159 seconds that a minimum of .1 of a second, or less, might have accompanied a maximum of only 30 seconds. In fact, such was observed in a few instances, the results, of course, being discarded, as the intervening charge could not be determined. Liberation within such a short interval was probably not always distinguished and hence appeared as doubles.

Suspecting this, an effort was made to increase the minimum time of discharge by decreasing the intensity of the ultra-violet light. This was done gradually until observations on droplet number 6 had been made. The decrease in the percentage of doubles seemed to verify the

Table I.

Drop No. 6.

t_g Secs.	t_F Secs.	No. of Charges on Drop.	No. of Charges Liberated.	Time for Liberation.	Change Number.	t_g Secs.	t_F Secs.	No. of Charges on Drop.	No. of Charges Liberated.	Time for Liberation.	Change Number.
3.6	1.4	3				4.2	1.2	3			
			1	20.4	1				1	64.4	15
	2.2	2					2.0	2			
			1	10.8	2				1	21.0	16
	8.2	1					5.4	1			
			1	7.5	3				1	5.6	17
	—	0					—	0			
3.7	1.2	3				4.4	1.2	3			
			1	47.5	4				2	36.2	18
	6.0	2					5.4	1			
			2	23.0	5				1	48.2	19
	—	0					—	0			
3.8	1.2	3				4.2	1.1	3			
			1	13.0	6				1	1.8	20
	2.0	2					1.9	2			
			1	5.0	7				1	24.2	21
	5.7	1					5.3	1			
			1	2.0	8				1	13.8	22
	—	0					—	0			
4.4	1.1	3				4.4	1.1	3			
			1	10.2	9				1	59.0	23
	1.8	2					1.8	2			
			1	14.8	10				1	3.0	24
	5.5	1					5.3	1			
			1	17.4	11				1	29.4	25
	—	0					—	0			
4.3	1.0	3					1.1	3			
			1	3.0	12				1	2.0	26
	2.0	2					1.9	2			
			1	10.5	13				1	25.2	27
	5.3	1					5.2	1			
			1	63.8	14				1	23.6	28
	—	0					—	0			
						4.1	1.1	3			
									1	10.2	29
							2.0	2			
									1	4.2	30
							5.3	1			
								0	1	7	31

Time of Observation = 1 hr. 10 min.
P. D. = 4,850 volts.
Number of Changes = 31
Number of Simultaneous " = 2 doubles

TABLE II.

Drop No. 13.

t_g Secs.	t_F Secs.	No. of Charges on Drop.	No. of Charges Liberated.	Time for Liberation.	Change Number.	t_g Secs.	t_F Secs.	No. of Charges on Drop.	No. of Charges Liberated.	Time for Liberation.	Change Number.
3.1	1.6	3					1.2	4			
			1	78.4	1				1	14.4	16
	3.1	2					1.5	3			
			1	19.5	2				1	19.5	17
	bal.	1					3.2	2			
			1	?	3				1	19.4	18
	—	0					bal.	1			
									1	61.0	19
							—	0			
3.0	1.1	4									
			1	113.0	4						
	1.7	3				3.0	.8	5			
			1	9.5	5				1	14.5	20
	3.0	2					1.2	4			
			1	17.4	6				1	50.4	21
	bal.	1					1.5	3			
			1	35.4	7				1	51.4	22
	—	0					3.2	2			
									2	62.0	23
							—	0			
3.1	1.1	4									
			1	12.2	8						
	1.7	3					.8	5			
			1	26.8	9				1	80.6	24
	3.1	2					1.2	4			
			1	112.0	10				1	73.5	25
	bal.	1					1.7	3			
			1	43.0	11				1	44.4	26
	—	0					3.0	2			
									1	5.4	27
							bal.	1			
	1.2	4							1	100.6	28
			1	9.8	12		—	0			
	1.6	3									
			1	60.5	13						
	3.2	2					.7	5			
			1	56.8	14				1	60.0	29
	bal.	1					1.2	4			
			1	9.0	15				1	111.4	30
	—	0					1.7	3			
									1	4.4	31
							3.1	2			

Time of Observation = 1 hr. 20 min.
P. D. = 4,760 volts.
Number of Changes = 31
Number of Simultaneous " = 1

Table III.

Drop No. 8.

t_g Secs.	t_F Secs.	No. of Charges on Drop.	No. of Charges Liberated.	Time for Liberation.	Change Number.	t_g Secs.	t_F Secs.	No. of Charges on Drop.	No. of Charges Liberated.	Time for Liberation.	Change Number.
4.6	1.0	3					1.0	3			
			1	9.2	1				1	43.8	16
	1.5	2					1.5	2			
			1	27.0	2				1	20.5	17
	4.5	1					4.5	1			
			1	37.0	3				1	5.4	18
	—	0					—	0			
4.8	1.0	3					0.9	3			
			1	26.0	4				1	6.2	19
	1.5	2					1.7	2			
			1	5.0	5				1	76.0	20
	4.5	1					4.7	1			
			1	61.6	6				1	10.0	21
	—	0					—	0			
	1.1	3									
			1	131.2	7						
	1.4	2									
			1	13.0	8						
	4.6	1									
			1	35.0	9						
	—	0									
5.0	.9	3									
			1	167.0	10						
	1.4	2									
			1	155.0	11						
	4.6	1									
			1	44.0	12						
	—	0									
4.9	1.0	3									
			1	23.0	13						
	1.5	2									
			1	179.0	14						
	4.5	1									
			1	5.0	15						
	—	0									

Time of Observation = 1 hr. 40 min.
P. D. = 4,730 volts
Number of Changes = 21
Number of Simultaneous " = 0

TABLE IV.

Drop No. 14.

t_g Secs.	t_F Secs.	No. of Charges on Drop.	No. of Charges Liberated.	Time for Liberation.	Change Number.	t_g Secs.	t_F Secs.	No. of Charges on Drop.	No. of Charges Liberated.	Time for Liberation.	Change Number.
4.4	1.0	4					1.4	3			
			1	14.6	1				1	35.4	9
	1.4	3					2.4	2			
			1	4.5	2				1	50.0	10
	2.2	2					9.0	1			
			1	31.0	3				1	6.0	11
	8.5	1					—	0			
			1	24.4	4						
	—	0									
						4.6	1.0	4			
									1	113.4	12
	1.0	4					1.5	3			
			1	113.0	5				1	32.0	13
	1.4	3					2.4	2			
			1	83.0	6				1	64.6	14
	2.2	2					8.6	1			
			1	36.2	7				1	29.8	15
	8.3	1					—	0			
			1	15.0	8						
	—	0									

Time of Observation = 1 hr.
P. D. = 4,000 volts.
Number of Changes = 15
Number of Simultaneous " = 0

TABLE V.

Results on Simultaneous Discharges.

Drop No.	t_g (Seconds).	$a \times 10^5$ (Cm.).	Discharges Observed.	Simultaneous Discharges	Per Cent. Simultaneous.	Charges on Droplet.	Time of Discharge (Seconds).		
							Maximum.	Minimum.	Mean.
1	2.9	4.23	21	4	19	0–3	24	1(?)	10
2	2.6	4.52	19	3	16	1–4	43	3(?)	12
3	3.2	4.05	17	2	12	1–3	60	2(?)	17
4	4.1	3.53	80	7	9	0–3	81	1(?)	16
5	2.1	5.08	36	3	8	1–6	45	3(?)	18
6	4.0	4.06	31	2	6.5	0–3	64	2(?)	21
7	2.3	4.86	13	0	0	2–6	252	3	110
8	4.8	3.22	21	0	0	0–3	167	5	50
9	1.9	5.32	18	0	0	1–5	182	1	48
10	4.1	3.54	7	0	0	0–4	143	2	48
11	3.7	3.75	6	0	0	0–3	73	16	32
12	2.3	4.80	57	2	3.5	1–5	159	0.5(?)	29
13	2.9	4.20	31	1	3.2	0–5	113	4(?)	43
14	4.4	3.89	15	0	0	0–4	113	4.5	43

TABLE VI.

Results on the Long Wave-Length Limit of Mercury.

Drop No.	t_g (Seconds).	$a \times 10^5$ (Cm.).	Wave-length ($\mu\mu$).	Discharges Observed.	Simultaneous Discharges.	Charges on Droplet.	Time of Discharge (Seconds).		
							Maximum.	Minimum.	Mean.
15	2.5	4.60	253.5	4	0	1–5	57	24	42
"	"	"	"	2	0	1–3	559	223	391[1]
16	3.8	3.68	312.6	0	0	4			(27 min.)
"	"	"	253.5	1	0	3–4			10 min.
17	2.2	4.91	253.5	3	0	2–4	454	240	347
"	"	"	312.6	0	0	4			(18 min.)

[1] Taken after 10 min. pause.

supposition; a very decided decrease was then given it and droplet number 7 gave no doubles. Thinking perhaps that this was a farther decrease in the intensity than was necessary, it was gradually increased until droplet number 12 had been observed, when doubles again appeared. Decreasing it again, they disappeared on droplet number 14.

The conclusion was drawn from this that a decrease in the illumination increased not only the maximum time of discharge but the minimum as well, and when it had reached a value of .5 of a second or more every change was distinguished and no doubles were recorded.

Hence it seems probable that in the photoelectric effect on mercury droplets two electrons are never liberated at the same time and that when two liberations appear to be simultaneous it is in reality two distinct liberations, the interval between them being too short for the observer to separate them. Since each droplet contains an enormous number of molecules, the results lend strong support to the point of view that in the photoelectric effect on mercury, simultaneous liberations from a given molecule do not occur.

THE LONG WAVE-LENGTH LIMIT OF MERCURY.

In this work a prism spectrometer was used to separate the spectral lines. Owing to the minuteness of the surface furnished by the droplets the lines were found too faint to give a rapid discharge even with the collimator slit open wide and the lamp operating on high energy. As may be seen from Table VI., no doubles appeared, but this was attributed more to the long times of discharge rather than to the single wave-length.

As to the long wave-length limit, liberations were obtained after long exposures from the strong line 253.5 $\mu\mu$. The next line tried was the strong one, 312.6 $\mu\mu$, and it gave no discharge. It was tried upon two

droplets each of which was tested by the line 253.5 $\mu\mu$ to make sure that the droplet was in the proper condition for discharging.

The lines between these were too faint to give results in a reasonable time, but it is evident that the long wave-length limit lies between 253.5 $\mu\mu$ and 312.6 $\mu\mu$.

I wish to thank Professor Millikan for suggesting and supervising these experiments and also my wife for her assistance in the experimental part.

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ON THE UNPOLARIZED FLUORESCENCE AND ABSORPTION OF FOUR DOUBLE CHLORIDES OF URANYL.

BY EDWARD L. NICHOLS AND H. L. HOWES.

IN a recent paper[1] an account was given of the fluorescence spectrum of ammonium uranyl chloride and more recently the polarized fluorescence and absorption of the four double chlorides, $UO_2Cl_2, 2NH_4Cl + 2H_2O$; $UO_2Cl_2 \cdot 2KCl + 2H_2O$; $UO_2Cl_2 \cdot 2RbCl + 2H_2O$ and $UO_2Cl_2 \cdot 2CsCl$ have been described and discussed.[2] Complete measurements of the fluorescence spectra and absorption spectra of this remarkable group of fluorescent compounds have since been completed and it is our purpose in the present paper to put these data on record and to consider their bearing upon the structure of fluorescence spectra and the relations between fluorescence and absorption.

As was shown in the paper on the polarized fluorescence, just cited, these four double chlorides have spectra which are partially resolved at + 20° and which exhibit an extraordinary similarity of structure. The departures from complete identity, moreover, are of such a nature as to reveal the relation of the more fully resolved bands obtained by excitation at low temperatures to those of the spectrum as observed at + 20°.

FLUORESCENCE BANDS AT + 20°.

The methods of locating the fluorescence bands were in the main those described in previous communications on the spectra of the uranyl compounds. Both photographic and visual measurements were made, thus checking the estimates of wave-length. Averages of the results of the two methods, which were in good agreement, have been used in the compilation of Table I. in which the wave-lengths and frequencies of all the fluorescence bands observed in the spectra of the four double chlorides at + 20° are given.

It is necessary to recognize the existence of eight groups of bands in these spectra although the terminal groups 1 and 8 are only visible under the most favorable conditions. Powerful excitation and freedom from stray light are necessary to bring out even the stronger bands in group 1,

[1] Nichols and Merritt, PHYS. REV. (2), VI., p. 358 (1915).

[2] Nichols and Howes, Proc. Nat. Acad. Sc., I., p. 444, and more fully in PHYS. REV. (2), VIII., p. 364 (1916).

TABLE I.

General List of the Fluorescence Bands in Spectra of the Double Uranyl Chlorides at + 20° C.

Group.	Series.	Potassium Uranyl Chloride.		Ammonium Uranyl Chloride.		Rubidium Uranyl Chloride.		Cæsium Uranyl Chloride.	
		λ.	$\frac{1}{\lambda}\times 10^3$.	λ.	$\frac{1}{\lambda}\times 10^3$.	λ.	$\frac{1}{\lambda}\times 10^3$.	λ.	$\frac{1}{\lambda}\times 10^3$.
	B			.6809	1469.7				
	C			.6716	1489.9				
1	*D*			.6635	1507.1				
	E			.6571	1521.8				
	A			.6501	1538.2				
	B	.6436	1553.7	.6430	1555.3	.6420	1557.6	.6401	1562.3
	C	.6375	1568.6	.6358	1572.9	.6354	1573.8	.6336	1578.3
2	*D*	.6303	1586.6	.6291	1589.6	.6281	1592.2	.6289	1590.1
	E	.6225	1606.4	.6231	1604.9	.6206	1611.3	.6219	1608.0
	A	.6171	1620.5	.6172	1620.2	.6162	1622.8[1]	.6156	1624.4
	B	.6111	1636.5	.6103	1638.6	.6098	1640.0	.6090	1642.0
	C	.6051	1652.5	.6041	1655.3	.6030	1658.3	.6015	1662.5
3	*D*	.5983	1671.5	.5978	1672.7	.5967	1675.9	.5970	1675.0
	E	.5919	1689.5	.5923	1688.2	.5903	1694.1	.5911	1691.9
	A	.5869	1704.0	.5866	1704.8	.5860	1706.4	.5854	1708.2
	B	.5816	1719.4	.5813	1720.3	.5800	1724.0	.5789	1727.4
	C	.5759	1736.4	.5752	1738.6	.5742	1741.6	.5729	1745.4
4	*D*	.5698	1754.9	.5696	1755.7	.5686	1758.7	.5689	1757.9
	E	.5642	1772.3	.5642	1772.3	.5625	1777.8	.5631	1775.9
	A	.5595	1787.2	.5593	1787.9	.5588	1789.4	.5587	1789.7
	B	.5551	1801.4	.5546	1803.1	.5537	1806.1	.5529	1808.6
	C	.5497	1819.3	.5492	1820.7	.5486	1822.8	.5472	1827.5
5	*D*	.5442	1837.6	.5436	1839.7	.5430	1841.5	.5433	1840.5
	E	.5390	1855.3	.5385	1856.9	.5377	1859.8	.5379	1859.1
	A	.5349	1869.6	.5342	1871.8	.5339	1873.1	.5339	1873.1
	B	.5306	1884.7	.5300	1886.8	.5291	1890.0	.5288	1891.1
	C	.5259	1901.5	.5250	1904.6	.5248	1905.5	.5234	1910.4
6	*D*	.5208	1920.1	.5200	1923.2	.5195	1925.0	.5198	1923.6
	E	.5159	1938.3	.5153	1940.5	.5145	1943.5	.5147	1942.7
	A	.5119	1953.5	.5112	1956.3	.5110	1957.1	.5113	1955.7
	B	.5078	1969.4	.5072	1971.5	.5066	1973.8	.5067	1973.5
	C	.5039	1984.4	.5031	1987.6	.5027	1989.1	.5024	1990.3
7	*D*	.4990	2004.0	.4986	2005.7	.4979	2008.4	.4989	2004.4
	E	.4946	2021.7	.4940	2024.1	.4935	2026.2	.4937	2025.6
	A	.4909	2036.9	.4904	2039.2	.4899	2041.4	.4904	2039.2
	B	.4869	2053.8	.4867	2054.6	.4857	2059.0	.4863	2056.3
	C	.4836	2068.0	.4829	2071.0	.4824	2072.8	.4819	2075.0
8	*D*								
	E								
	A								

which lies in the full red of the spectrum. The weaker terminal bands of the group which have an intensity of less than 1 per cent. of that of the crest are almost or quite invisible. Long exposures of photographic plates specially sensitized for red afford the best method for this part of the spectrum.

In group 8 the difficulties are scarcely less serious on account of the overlapping of fluorescence and absorption. Fortunately the frequency intervals for the various series having been established, one may supplement, with considerable assurance, the missing values by computation and this has been done, where necessary. Computed values are indicated as such wherever they appear in the tables.

Fluorescence series are designated as *B*, *C*, *D*, *E*, *A*, instead of the *b*, *c*, *d*, *e* and *a* used in the papers on the polarized spectra, already cited. The small letters are reserved for the indication of the related absorption series, which were formerly denoted by Greek characters.[1]

By means of the data in Table I. the conclusions reached in the previous study of the ammonium uranyl chloride may be extended to all four of the double chlorides now under consideration.

These conclusions are as follows:

1. In all four salts the fluorescence series, *B*, *C*, *D*, *E*, *A* have constant frequency intervals; *i. e.*, there is no indication in passing from group 1 to group 8 of a change in the interval of sufficient size to be detected.

2. The interval is essentially the same for the potassium, ammonium and rubidium chlorides but appears to be somewhat smaller in the case of the cæsium chloride. It will be shown in a later paragraph that the discrepancy is only an apparent one.

3. The interval is nearly the same for different series but the evidence from these measurements while not in itself conclusive seems to indicate small but real variations. The strongest indication is found in the *C* series which has the lowest average interval.

THE DISTANCES BETWEEN GROUPS.

Since it is at least approximately true that all the fluorescence series are series of constant interval and that in each salt the groups are identical as to the arrangement of the bands, it is of interest to treat the groups as units.

To determine the distances between groups, what may be termed the center of each group was found by averaging the frequencies of the five bands. The location of these centers and the intervals, for groups 2, 3,

[1] Two series, however, which come into coincidence with members of the *B* and *C* fluorescence series respectively in group 8 instead of in group 7 have been designated as β and γ.

4, 5, 6 and 7 are given in Table II. Groups 1 and 8 for which insufficient data are available are omitted, except in the case of the ammonium chloride.

TABLE II.

Distances between Fluorescence Groups.

Group.	Potassium Uranyl Chloride.		Ammonium Uranyl Chloride.		Rubidium Uranyl Chloride		Cæsium Uranyl Chloride.	
	Center of Group.	Interval.	Center of Group.	Interval.	Center of Group.	Interval.	Center of Group.	Interval.
1			1505.3					
				83.3				
2	1587.2		1588.6		1591.5		1592.6	
		83.6		83.3		83.4		83.3
3	1670.8		1671.9		1674.9		1675.9	
		83.2		83.1		83.4		83.4
4	1754.0		1755.0		1758.3		1759.3	
		82.6		83.4		82.4		82.5
5	1836.6		1838.4		1840.7		1841.8	
		83.0		83.9		83.5		82.9
6	1919.6		1922.3		1924.2		1924.7	
		83.7		83.3		83.6		81.9
7	2003.3		2005.6		2007.8		2006.6	
Average distances		83.22		83.38		83.26		82.80

The results bring out clearly the uniformity of interval throughout the spectrum for each substance and the essential identity of structure in the spectra of the first three salts. The only departure from uniformity is in the cæsium chloride, where the average interval is unmistakably lower and where there is a suggestion of a diminishing interval from red towards violet. It will be seen later that this apparent departure from the law of constant intervals, a law which characterizes the fluorescence of all the uranyl compounds, is due to the effects of absorption and to the fact that we are dealing with complex bands.

THE ARRANGEMENT OF BANDS WITHIN THE GROUPS.

To the eye the fluorescence spectra under consideration appear to consist of an assemblage of evenly spaced bands which vary periodically in intensity so as to form a succession of similar groups. This is not strictly the case, however, as may be shown by comparing the frequencies of the bands in a given group. The average distances between neighboring bands, thus obtained from the data in Table I. are presented in Table III.

TABLE III.

Average Distances between Neighboring Bands in the Fluorescence Spectrum at + 20° C.

Fluorescing Substance.	Average Distances.				
	C—B.	*D—C.*	*E—D.*	*A—E.*	*B—A.*
$UO_2Cl_2 \cdot 2KCl$	15.97	18.66	17.96	14.70	15.58
$UO_2Cl_2 \cdot 2NH_4Cl$	17.56	17.74	17.86	15.67	15.67
$UO_2Cl_2 \cdot 2RbCl$	16.20	18.43	18.50	12.75	17.12
$UO_2Cl_2 \cdot 2CsCl$	18.25	12.85	18.63	14.52	18.10
General Averages	16.99	16.92	18.24	14.41	16.62

In the rubidium spectrum bands A and E are crowded together and in the cæsium spectrum D and C are similarly much nearer to one another than are the other pairs of bands. It will be noticed further that the average distance between A and E is less for all four chlorides than the other average distances.

The arrangement of bands within the group, in the four spectra, is conveniently compared by means of the diagram in Fig. 1, in which the

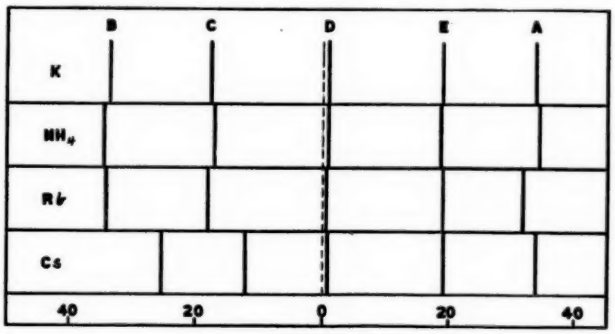

Fig. 1.

centers of the groups are in the same vertical (dotted) line. It will be seen from the diagram:

1. That the group center is in all cases almost coincident with the crest of the D band.

2. That the arrangement of the bands within the group is essentially the same in all, except for the marked displacement of A in the spectrum of rubidium chloride and of B and C in that of the cæsium chloride, as mentioned above.

The explanation of these discrepancies involves a consideration of the effect of cooling upon the spectra and will be found in a later paragraph of this paper.

INTERVALS OF THE INDIVIDUAL SERIES.

The average interval for each series has been computed by obtaining the differences between the observed frequency of each band and the frequencies of all the other bands of the series and dividing the sum by the total number of intervals in question (see Table IV.).

Here as in averaging by groups we must leave the question of the reality of the apparent but small differences in the intervals of the various series and of the various salts to be determined from the study of the more completely resolved bands at the temperature of liquid air.

TABLE IV.

Average Intervals by Series at + 20° C.

Series.	K.	NH_4.	Rb.	Cs.	Averages by Series.
B	83.42	83.34	83.49	82.32	83.14
C	83.11	82.99	82.97	82.50	82.89
D	83.30	83.21	83.17	82.85	83.13
E	83.00	83.81	82.97	83.45	83.31
A	83.23	83.65	83.77	82.85	83.37
Averages	83.21	83.40	83.27	82.80	83.17

INFLUENCE OF MOLECULAR WEIGHT UPON THE POSITION OF FLUORESCENCE BANDS.

While the determinations thus far described may be deemed indecisive as to small differences of interval, the influence of molecular weight upon the *position* of bands in the spectrum is unmistakable. In Table I. the fairly regular increase in frequency of each band as we pass from potassium to cæsium is sufficiently evident. In Fig. 2 this general shift, which is present in all the groups and affects all series, can be seen at a glance.

Almost the only reversed shifts occur in the case of those bands of the spectrum of the cæsium chloride which show anomolous placing in the spectral groups. In Table II., where the accidental errors pertaining to individual bands are submerged in the process of averaging, the shift is still more systematic.

Ignoring group 7, in which the bands are more or less displaced by absorption, we find the following values for the shift.

Shift of the Groups (K to Cs).

Group	2	3	4	5	6
Shift	5.4	5.1	5.3	5.2	5.2

Average shift from K to Cs 5.2.

The shift is therefore *approximately uniform throughout the spectrum.* If all of the series were of the *same* constant frequency interval these shifts would be the same.

The shift is much greater between NH_4 and Rb than between K and NH_4 or between Rb and Cs, the averages being as follows:

Average Shift of Groups.

K to NH_4	1.3
NH_4 to Rb	2.9
Rb to Cs	1.6

In this discussion, as in the consideration of the same effect in the case of the polarized spectra of these chlorides[1] the order of the molecular weights used is K, NH_4, Rb, Cs. This is in accordance with the results

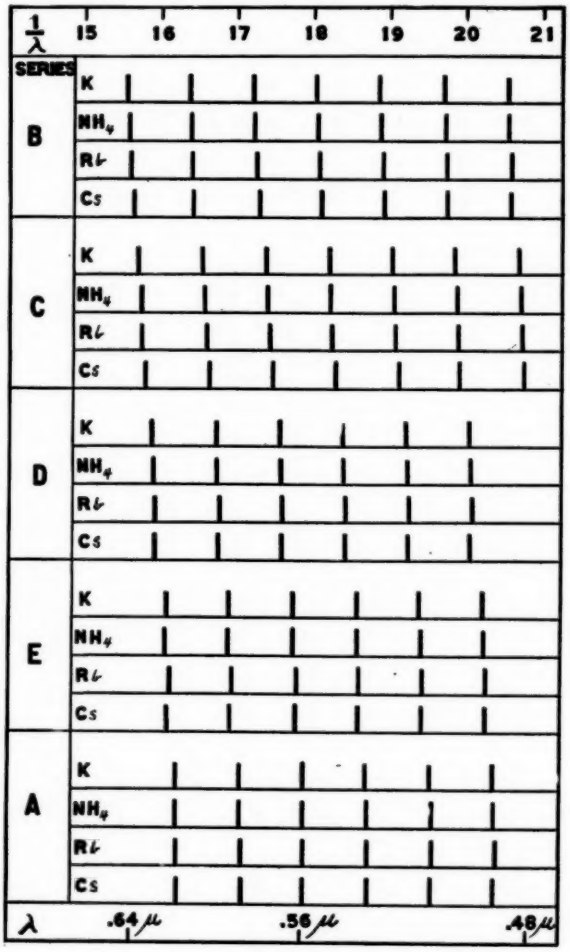

Fig. 2.

of Tutton[2] who has shown that whenever the optical constants of crystals vary with the molecular weights, NH_4 lies between K and Rb; as though its effective molecular weight were larger instead of being smaller than that of K.

The Effects of Temperature.

Although the results obtained by exciting ammonium uranyl chloride at the temperature of liquid air have already been published, as have the

[1] Nichols and Howes, l. c.

[2] Tutton, A. E., Crystalline Structure and Chemical Constitution (London, 1916).

TABLE V.

General List of the Fluorescence Bands in Spectra of the Double Uranyl Chlorides at − 185° C.

Group.	Series.	Potassium Uranyl Chloride.		Ammonium Uranyl Chloride.		Rubidium Uranyl Chloride.		Cæsium Uranyl Chloride.	
		λ.	$\frac{1}{\lambda}\times 10^3$.	λ.	$\frac{1}{\lambda}\times 10^3$.	λ.	$\frac{1}{\lambda}\times 10^3$.	λ.	$\frac{1}{\lambda}\times 10^3$.
	B_2			.6398	1563.0				
2	C_2			.6330	1579.8				
	D_2			.6283	1591.5				
	E_2''			.6207	1611.0				
	B_1			.6110	1636.7				
	B_2			.6079	1645.0			.6056	1651.3
3	C_2	.6035	1657.0	.6016	1662.1	.6018	1661.7	.5991	1669.2
	D_1	.6006	1665.0			.5990	1669.4	.5964	1676.7
	D_2			.5968	1675.6				
	E_2''			.5899	1695.0				
	B_2	.5803	1723.2	.5791	1726.9			.5764	1734.9
	C_1							.5721	1747.9
	C_2	.5752	1738.4	.5733	1744.4	.5731	1745.0	.5705	1752.7
	D_1	.5724	1747.0	.5704	1753.1	.5703	1753.4	.5684	1759.4
4	D_2			.5677	1761.4			.5652	1769.3
	E_2'	.5641	1772.7						
	E_2''			.5624	1778.1				
	A_1	.5603	1784.6	.5595	1787.3				
	A_2					.5573	1794.5	.5564	1797.2
	B_1	.5569	1795.8			.5546	1803.1	.5526	1809.5
	B_2	.5542	1804.4	.5524	1810.4	.5520	1811.5	.5500	1818.1
	C_1	.5508	1815.5	.5493	1820.5	.5489	1821.9	.5464	1830.2
	C_2	.5489	1821.7	.5471	1827.7	.5471	1827.8	.5452	1834.1
	D_1'							.5440	1838.2
5	D_1	.5461	1831.0	.5445	1836.7	.5444	1836.9	.5427	1842.5
	D_2'							.5412	1847.7
	D_2	.5437	1839.4	.5420	1845.1	.5419	1845.2	.5395	1853.7
	E_2'	.5389	1855.7	.5379	1859.0				
	E_2''			.5370	1862.0			.5358	1866.4
	A_1	.5354	1867.6	.5345	1870.8				
	A_2					.5326	1877.7	.5318	1880.4
	B_1	.5321	1879.5			.5300	1886.8	.5286	1891.8
	B_2	.5297	1888.0	.5279	1894.4	.5277	1895.0	.5260	1901.1
	B_3	.5279	1894.3						
	C_1	.5262	1900.4	.5250	1904.8	.5247	1905.9	.5223	1914.6
6	C_2	.5250	1904.6	.5234	1910.6	.5231	1911.7	.5214	1918.0
	D_1'							.5201	1922.7
	D_1	.5226	1913.5	.5206	1921.0	.5207	1920.3	.5191	1926.3
	D_2'							.5179	1930.9

Group.	Series.	Potassium Uranyl Chloride.		Ammonium Uranyl Chloride.		Rubidium Uranyl Chloride.		Cæsium Uranyl Chloride.	
		λ.	$\frac{1}{\lambda}\times 10^3$.	λ.	$\frac{1}{\lambda}\times 10^3$.	λ.	$\frac{1}{\lambda}\times 10^3$.	λ.	$\frac{1}{\lambda}\times 10^3$.
	D_2	.5200	1922.9	.5184	1929.2	.5182	1929.9	.5163	1937.0
	E_2'	.5155	1939.9	.5149	1941.9			.5137	1946.8
6	E_2''			.5141	1945.0			.5127	1950.4
Cont.	A_1	.5124	1951.6	.5118	1953.7	.5107	1957.9		
	A_2					.5098	1961.6	.5092	1963.9
	B_1	.5092	1963.9	.5080	1968.7	.5073	1971.4	.5059	1976.5
	B_2	.5070	1972.3	.5056	1977.9	.5054	1978.6	.5038	1984.9
	B_3	.5056	1977.8						
	C_1			.5028	1988.7			.5006	1997.6
	C_2	.5031	1987.6	.5018	1992.7	.5018	1993.0		
	D_1	.5007	1997.2	.4989	2004.5	.4991	2003.7	.4979	2008.5
7	D_2'							.4963	2014.9
	D_2	.4982	2007.4	.4967	2013.4	.4967	2013.2	.4950	2020.2
	E_1	.4956	2017.8			.4938	2025.1		
	E_2'			.4940	2024.1			.4926	2030.0
	E_2''							.4918	2033.3
	A_1'	.4930	2028.4			.4917	2033.8		
	A_1	.4916	2034.2			.4902	2040.0		
	A_2	.4904	2039.2						
8	B_1							.4857	2058.9

effects of cooling upon the polarized spectra of the four double chlorides, it has seemed desirable to record here the measurements subsequently made upon the unpolarized spectra at low temperatures. Future students of this subject are perhaps more likely to deal with the unpolarized spectra on account of the difficulty in procuring crystals that yield the polarized bands satisfactorily. It is moreover of interest to compare the mode of resolution for the different chlorides.

The positions of the bands in Table V. are from observations upon the spectra when excitation occurs at $-185°$. The nomenclature is intended to indicate as far as possible the relation of the bands at $-185°$ to those at $+20°$; B_1, B_2, etc., denoting components of B, etc., which have been rendered visible by the resolution effected by cooling.

The explanation offered in the paper on the ammonium uranyl chloride (pp. 366 and 369) to account for the very large temperature shifts applies equally well to the potassium and rubidium salts. It was based on the observation, at intermediate temperatures, that each band at $+20°$ is an unresolved doublet the components of which are in general of unequal intensity. The effect of cooling is to resolve these doublets and at the same time to weaken one component and strengthen the other. The

weakened component sometimes disappears altogether or more frequently remains visible only in the strongest groups. In the case of cæsium uranyl chloride the relations are complicated by the further resolution of these components so that the connection with the original complexes is less easily traced.

To indicate the general character of these resolutions and the apparent temperature shift which results therefrom the positions of the bands of group 6 at − 185° are plotted for all four chlorides (see Fig. 3). Intensities of the − 185° bands are indicated roughly by the height of the lines. The corresponding crests of the bands at + 20° are represented by dotted lines. Group 6 was selected because it offers better examples of the further breaking up of the components and of other phases of the process of resolution than do groups towards the red in which resolution is progressively less complete.

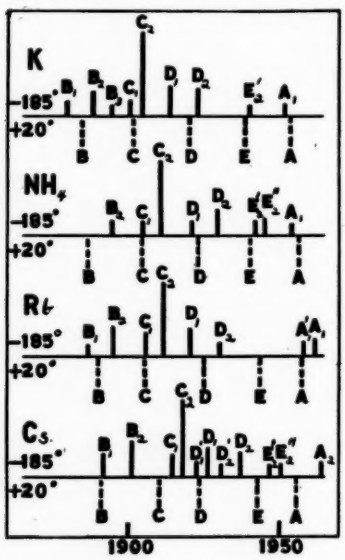

Fig. 3.

Two questions which were left undetermined in the study of the spectra at + 20° may be regarded as settled by these measurements of the bands at − 185°.

1. That the intervals are not the same for all series in a given spectrum is clearly established. For example the components C_1, C_2 which take the place of the C bands in all four spectra have distinctly different intervals, *i. e.*, 84.00 for C_1 and 82.75 for C_2. It is noteworthy that C_2, which becomes the crest of the group in place of C, also has the small interval.

It might be questioned whether these so-called components are not merely accidental neighbors rather than products of the same vibrating system, but for the fact that they are present in all the spectra and have very nearly if not precisely the same relative positions to each other in all.

2. The average interval of all series in the spectrum of the cæsium chloride (82.80) at + 20° which causes the notable displacement of the bands of that substance, becomes 83.44 when we take the average of the intervals of the bands at − 185°. That is to say it is, within the errors of observation, the same as the general average for the other salts. On the basis of the measurements at low temperatures (see Table VI.), we must conclude that the four double chlorides have approximately the same average frequency interval.

TABLE VI.

Average Intervals of the Fluorescence Series at − 185° C.

Series.	K.	NH_4.	Rb.	Cs.	Average.
B_1.....	83.9	83.0	84.2	83.0	83.53
B_2.....	83.1	83.2	83.6	83.4	83.33
B_3.....	83.5				
C_1.....	84.9	84.1	84.0	83.7	84.18
C_2.....	82.7	82.7	82.9	82.8	82.78
D_1.....	83.1	83.8	83.6	83.1	83.40
D_1'.....				84.5	
D_2.....	84.1	84.2	84.0	83.6	83.98
D_2'.....				83.6	
E_2'.....	83.6	82.5		83.2	83.10
E_2''.....		83.3		83.5	83.40
A_1.....	83.3	83.1	82.1		82.83
A_2.....			83.6	83.4	83.50
	83.58	83.32	83.50	83.44	

THE ABSORPTION SPECTRA.

A glance at the absorption spectra of the double chlorides, obtained by viewing through a spectroscope the light transmitted by the crystals at room temperature, shows the same higher degree of resolution that characterizes the fluorescence spectra of these salts. The salient feature is a series of strong, rather narrow bands, equally spaced, as to frequency, like the broader bands of the other uranyl compounds. The interval, as in all uranyl absorption spectra, is distinctly smaller than the fluorescence interval. Between these are several series of weaker bands.

The complete mapping of the absorption spectra is difficult. It cannot be done visually since the bands extend out into the darkness of the ultra-violet. Photography adds considerable detail but does not greatly extend the range towards the shorter wave-lengths on account of the rapidly increasing opacity. In the brighter regions of the spectrum, on the other hand, more can be seen with the eye than can be found on the photographic plate.

The data which we have obtained and which are presented in the following tables have been procured by using both methods.

A great variety of light filters and combinations of light filters have been employed in different parts of the spectrum, with widely different exposures for the strong and weak bands. The thickness of the transmitting layer has likewise been varied as far as the available material

TABLE VII.

General List of Bands in the Absorption Spectra of the Double Uranyl Chlorides at + 20° C.

Potassium Uranyl Chloride.				Ammonium Uranyl Chloride.			
Group.	Series.	λ.	$\frac{1}{\lambda} \times 10^3$.	Group.	Series.	λ.	$\frac{1}{\lambda} \times 10^3$.
	B	.5549	1802.1		*B*	.5548	1802.5
	C	.5494	1820.2		*C*	.5492	1820.8
	D	.5445	1836.5		*D*	.5438	1838.9
5	*c*	.5417	1846.0	5	*c*	.5409	1848.8
	E	.5390	1855.3		*E*	.5383	1857.8
	d	.5362	1865.0		*d''*	.5350	1869.2
	A	.5351	1869.0		*A*	.5342	1871.8
	e	.5322	1879.0		*B*	.5301	1886.5
	B	.5305	1885.1		*C*	.5246	1906.2
	C	.5257	1902.2	6	*D*	.5197	1924.2
6	*D*	.5206	1920.9		*E*	.5149	1942.3
	E	.5161	1937.6		*A*	.5109	1957.4
	A	.5116	1954.7		*b*	.5076	1970.1
					c	.5029	1988.5
	b	.5076	1970.1		*γ*	.4996	2001.6
	c	.5037	1985.2	7	*d''*	.4978	2008.9
7	*γ*	.5008	1997.0		*e*	.4942	2023.3
	d	.4989	2004.3		*b*	.4899	2041.2
	e	.4947	2021.4				
	b	.4906	2038.5		*c*	.4860	2057.5
				8	*γ*	.4829	2070.6
	c	.4869	2053.8		*d''*	.4808	2080.1
8	*γ*	.4837	2067.4		*e*	.4776	2094.0
	d	.4819	2075.1				
	e	.4783	2090.9		*b*	.4733	2113.0
					c	.4704	2126.0
	b	.4742	2108.8	9	*γ*	.4667	2142.6
	c	.4705	2125.4		*d''*	.4652	2149.5
9	*γ*	.4679	2137.0		*e*	.4618	2165.5
	d	.4659	2146.4		*e''*	.4601	2173.5
	e	.4627	2161.0				
					b	.4577	2185.0
	b	.4588	2179.6	10	*d*	.4507	2218.9
10	*d''*	.4501	2221.8		*e''*	.4455	2244.5
					b	.4432	2256.2
	b	.4449	2247.8	11	*d*	.4370	2288.5
11	*d''*	.4363	2291.9		*e*	.4331	2309.0
	e''	.4323	2313.0		*e''*	.432	2314.6
					b	.4293	2329.5
	a''	.4293	2329.4	12	*d*	.4237	2359.9
12	*d''*	.4235	2361.3		*e*	.4202	2379.9
	e''	.4199	2381.6		*e''*	.4194	2384.6

TABLE VII.—*Continued.*

Potassium Uranyl Chloride.				Ammonium Uranyl Chloride.			
Group.	Series.	λ.	$\frac{1}{\lambda}\times 10^3$.	Group.	Series.	λ.	$\frac{1}{\lambda}\times 10^3$.
	a''	.4169	2398.7				
	d''	.4113	2431.5		*b*	.4166	2400.3
13	*e*	.4095	2442.0	13	*d*	.4112	2432.0
	e''	.4077	2452.8		*e''*	.4073	2455.2
	d''	.3995	2503.1		*d*	.3997	2501.8
14	*e''*	.3962	2524.0	14	*e''*	.3957	2527.4
	a''	.3938	2539.4		*γ*	.3899	2565.1
15	*γ*	.3906	2560.2	15	*d*	.3885	2573.7
	d''	.3884	2574.8		*e*	.3863	2588.7
	b	.3842	2603.0		*b''*	.3815	2620.9
16	*c*	.3811	2623.8	16	*γ*	.3792	2637.1
	d'	.3789	2638.9		*e*	.3757	2661.7
	b	.3738	2675.0		*b''*	.3714	2692.8
17	*c*	.3713	2693.3	17	*γ*	.3692	2708.6
	d'	.3687	2712.2		*d'*	.3685	2713.7
					e''	.3648	2741.2
				18	*b*	.3627	2756.8

Rubidium Uranyl Chloride.				Cæsium Uranyl Chloride.			
Group.	Series.	λ.	$\frac{1}{\lambda}\times 10^3$.	Group.	Series.	λ.	$\frac{1}{\lambda}\times 10^3$.
	C	.5747	1740.0	4	*A*	.5582	1791.5
4	*E*	.5622	1778.7				
	A	.5588	1789.5		*B*	.5531	1808.0
					C	.5467	1829.2
	B	.5537	1806.1		*D*	.5426	1843.0
	C	.5485	1823.2	5	*β*	.5416	1846.4
	b	.5450	1834.9		*E*	.5373	1861.2
5	*D*	.5430	1841.6		*A*	.5339	1873.0
	E	.5377	1859.8		*B*	.5289	1890.7
	A	.5342	1872.0		*C*	.5233	1911.1
				6	*D*	.5198	1923.8
	B	.5294	1889.0		*E*	.5143	1944.4
	C	.5243	1907.2		*A*	.5108	1957.8
	D	.5190	1926.7				
6	*d*	.5150	1941.7?		*b*	.5065	1974.2
	E	.5144	1944.0		*c*	.5017	1993.1
	e	.5123	1952.0?	7	*d*	.4999	2004.9
	A	.5105	1958.7		*e*	.4937	2025.6
					a	.4909	2037.1
					b	.4894	2043.3

Rubidium Uranyl Chloride.				Cæsium Uranyl Chloride.			
Group.	Series.	λ.	$\frac{1}{\lambda}\times 10^3$.	Group.	Series.	λ.	$\frac{1}{\lambda}\times 10^3$.
	b	.5066	1974.0		*β*	.4864	2056.0
	c	.5028	1989.1		*c*	.4844	2064.4
	γ	.4996	2001.6	8	*d'*	.4828	2071.3
7	*d*	.4982	2007.1		*d*	.4816	2076.3
	d''	.4966	2013.7		*e*	.4774	2094.7
	e	.4938	2025.3				
	b	.4892	2044.0		*b*	.4731	2113.9
	c	.4860	2057.6	9	*β*	.4701	2127.1
	γ	.4830	2070.5		*d*	.4661	2145.5
8	*d*	.4808	2080.1		*e*	.4618	2165.6
	e	.4776	2094.0				
					b	.4578	2184.3
	b	.4729	2114.4	10	*β*	.4547	2199.3
	c	.4694	2130.4		*d'*	.4520	2212.2
9	*γ*	.4670	2141.3		*e*	.4497	2237.0
	d	.4653	2149.2				
	e	.4616	2166.4		*b*	.4434	2255.3
	b	.4578	2184.6	11	*β*	.4406	2269.6
	c	.4547	2199.3		*d'*	.4378	2284.0
10	*γ*	.4527	2209.0		*e*	.4329	2310.0
	d''	.4492	2226.0				
	e	.4473	2235.6		*b*	.4297	2327.0
	e''	.4447	2248.5	12	*d'*	.4247	2354.6
					e	.4205	2378.2
	b	.4434	2253.1				
11	*d*	.4361	2293.1		*b*	.4169	2398.4
	e''	.4314	2318.0	13	*β*	.4147	2411.4
	a''	.4285	2333.7		*d'*	.4121	2426.6
12	*d*	.4229	2364.8		*e*	.4085	2448.0
	a''	.4160	2403.9				
	γ	.4126	2423.7		*b*	.4047	2471.0
13	*d*	.4106	2435.4	14	*d'*	.4006	2496.6
	e''	.4065	2460.0		*e*	.3968	2520.2
	a''	.4046	2471.6		*b*	.3940	2539.7
	γ	.4011	2493.1	15	*d'*	.3893	2568.7
14	*d*	.3994	2503.9		*a*	.3843	2602.2
	e''	.3956	2527.8				
	a''	.3934	2542.1		*β*	.3816	2620.5
15	*d*	.3879	2577.7	16	*d'*	.3793	2636.8
	e	.3858	2592.0		*a*	.3739	2674.2
	b	.3837	2606.5				
16	*c*	.3810	2624.5	17	*β*	.3715	2691.8
	d'	.3785	2642.0				
17	*b*	.3732	2679.5				

TABLE VIII.

General List of Bands in the Absorption Spectra of the Double Uranyl Chlorides at − 185° C.

Potassium Uranyl Chloride.				Ammonium Uranyl Chloride.			
Group.	Series.	λ.	$\frac{1}{\lambda} \times 10^3$.	Group.	Series.	λ.	$\frac{1}{\lambda} \times 10^3$.
	E_2'	.5150	1941.7		E_2''	.5139	1945.9
6	e_1	.5134	1947.6	6	A_1	.5119	1953.5
	e_2'	.5116	1954.7			.5111	1956.6
	b_1'	.5101	1960.4		e_2''	.5093	1963.5
	a_2	.5087	1965.8		B_1	.5082	1967.7
	b_2	.5070	1972.4		b_2'	.5067	1973.6
	b_3	.5057	1977.5		B_2	.5058	1977.1
	c_2'	.5038	1984.9		b_2''	.5048	1981.0
7	c_2''	.5027	1989.3	7	b_3	.5038	1984.9
	d_1	.5005	1998.0		c_2	.5020	1992.0
	d_2	.4978	2008.8				1996.8
	d_3	.4965	2014.0		d_1'	.5008	2002.8
	e_2'	.4942	2023.4		d_1''	.4983	2006.8
	b_1'	.4928	2029.1		d_2''	.4965	2014.1
	a_2	.4907	2038.1		e_2''	.4924	2031.0
	b_2	.4893	2043.6		b_1	.4906	2038.5
	c_2	.4860	2057.6		b_2'	.4889	2045.5
8	d_1	.4834	2068.8		b_2''	.4875	2051.1
	d_2	.4810	2079.0		b_3	.4863	2056.5
	e_2'	.4774	2094.5	8	c_2	.4843	2064.7
					d_1''	.4813	2077.9
	b_1'	.4760	2100.8		d_2''	.4792	2086.8
	a_2	.4743	2108.5		e_1	.4778	2092.7
	b_2	.4731	2113.7		e_2''	.4756	2102.4
9	c_2	.4701	2127.4				
	d_1	.4674	2139.5		b_1	.4742	2109.0
	d_2	.4654	2148.9		b_2'	.4724	2116.9
	d_3	.4640	2155.2		b_2''	.4711	2122.7
	e_2'	.4619	2165.0	9	c_2	.4681	2136.5
					d_1''	.4653	2148.9
	b_1'	.4606	2170.9		d_2''	.4639	2155.5
	a_2	.4589	2178.9		e_1	.4625	2162.1
	b_2	.4579	2184.0		e_2''	.4599	2174.4
10	c_2	.4551	2197.3				
	d_1	.4528	2208.5		b_1	.4587	2180.2
	d_2	.4510	2217.1		b_2'	.4571	2187.7
	e_1	.4485	2229.4		b_2''	.4560	2193.1
					b_3	.4551	2197.3
	b_2	.4436	2254.3	10	c_2	.4530	2207.3
	c_2'	.4417	2264.2		d_1''	.4508	2218.2
11	d_1	.4389	2278.5		d_2''	.4490	2227.0
	d_2	.4371	2287.6		e_1	.4478	2233.0
	e_2'	.4337	2305.5		e_2''	.4460	2242.2

TABLE VIII.—*Continued.*

Potassium Uranyl Chloride.				Ammonium Uranyl Chloride.			
Group.	Series.	λ.	$\frac{1}{\lambda}\times 10^3$.	Group.	Series.	λ.	$\frac{1}{\lambda}\times 10^3$.
	a_2	.4311	2319.6		b_1	.4443	2250.9
	b_2	.4300	2325.6		b_2''	.4413	2265.9
	c_2'	.4287	2332.7		c_2	.4389	2278.3
	c_2	.4277	2337.8	11	d_1''	.4370	2288.5
12	c_2''	.4262	2346.1		d_2''	.4352	2298.0
	d_2	.4244	2356.1		e_1	.4341	2303.4
	d_3	.4232	2362.7				
	e_1	.4221	2369.1		b_1	.4305	2322.8
	e_2'	.4211	2374.9		b_2''	.4277	2338.2
					c_2	.4259	2348.1
	a_1	.4194	2384.4	12	d_1''	.4239	2359.1
	a_2''	.4181	2391.9		d_2''	.4222	2368.3
	c_2'	.4160	2404.0		e_1	.4209	2376.0
13	c_2''	.4141	2414.9		e_2''	.4188	2387.5
	d_2	.4116	2429.2				
	d_3	.4105	2436.3		b_1	.4177	2394.0
	e_1	.4097	2441.0		b_2''	.4152	2408.7
					b_3	.4146	2411.9
	a_1	.4071	2456.4	13	c_2	.4134	2419.0
14	e_1	.3983	2510.6		d_1''	.4114	2430.9
	e_2'	.3971	2518.3		d_2''	.4102	2437.9
					e_1	.4090	2445.0
	a_1	.3959	2525.6		e_2''	.4066	2459.7
	a_2''	.3947	2533.3				
15	c_2'	.3933	2542.3		b_1	.4054	2466.8
	d_2	.3893	2568.7		b_2''	.4034	2479.0
	e_1	.3873	2582.0		b_3	.4028	2482.5
				14	c_2	.4016	2489.9
	a_1	.3854	2594.7		d_1''	.3997	2502.0
16	a_2''	.3835	2607.5		e_1	.3975	2515.8
					e_2''	.3951	2530.7
					b_1	.3941	2537.3
					b_2''	.3921	2550.1
				15	c_2	.3904	2561.6
					d_1''	.3886	2573.2
					b_1	.3833	2609.0
					b_2''	.3813	2622.7
					b_3	.3808	2626.3
				16	c_2	.3798	2633.0
					d_1''	.3780	2645.5
					d_2''	.3774	2650.0
					e_1	.3763	2657.5

Rubidium Uranyl Chloride.				Cæsium Uranyl Chloride.			
Group.	Series.	λ.	$\frac{1}{\lambda} \times 10^3$.	Group.	Series.	λ.	$\frac{1}{\lambda} \times 10^3$.
	d_2''	.5143	1944.4		d_2''	.5118	1953.9
	e_1'	.5122	1952.4			.5111	1956.6
		.5116	1954.7	6	e_2'	.5105	1958.9
	A_1	.5107	1958.1		a_1'	.5084	1967.0
6	a_1'	.5092	1963.9			.5074	1970.8
	b_1''	.5066	1973.9				
	b_2	.5048	1981.0		b_1'	.5065	1974.3
		.5036	1985.7		b_1''	.5055	1978.2
	c_2	.5011	1995.6		b_2'	.5043	1982.9
	D_1	.4987	2005.2		b_2''	.5031	1987.7
	d_2'	.4975	2010.1		b_3	.5022	1991.3
7	d_2''	.4960	2016.1		C_1	.5006	1997.6
	e_1'	.4947	2021.6	7	c_2	.4986	2005.6
	e_2	.4924	2030.7		d_1	.4976	2009.6
	a_1'	.4909	2036.9		D_2'	.4960	2016.1
					d_2''	.4945	2022.2
	b_1''	.4892	2044.2		e_2'	.4927	2029.6
	b_2	.4877	2050.4		e_2''	.4916	2034.1
	c_1	.4856	2059.3		a_1'	.4907	2038.1
	c_2	.4843	2064.7				
8	d_1	.4818	2075.4		b_1'	.4889	2045.3
	d_2''	.4792	2086.8		b_2'	.4874	2051.6
	e_1'	.4776	2093.6		b_3	.4850	2061.9
	e_2	.4760	2101.0		c_1'	.4844	2064.3
	a_1'	.4745	2107.5		c_1	.4836	2067.8
				8	d_1''	.4804	2081.6
	b_1''	.4728	2114.9		d_2'	.4793	2086.2
	b_2	.4714	2121.4		d_2''	.4778	2092.7
	c_1	.4692	2131.3		e_2'	.4761	2100.4
	c_2	.4685	2134.5		e_2''	.4749	2105.5
9	d_1	.4660	2145.7		a_1'	.4743	2108.4
	d_2''	.4633	2158.2				
	e_1	.4615	2166.8		b_1'	.4725	2116.4
	e_2	.4603	2172.5		b_2'	.4710	2122.9
	a_1'	.4591	2178.2		c_1'	.4684	2134.9
					c_2'	.4670	2141.3
	b_1''	.4577	2184.9		d_1''	.4646	2152.4
	b_2	.4563	2191.6	9	d_2'	.4637	2156.4
	c_1	.4545	2200.0		d_2''	.4621	2163.8
	c_2	.4534	2205.4		e_2'	.4607	2170.6
10	d_1	.4515	2214.9		e_2''	.4595	2176.1
	d_2'	.4502	2221.4		a_1'	.4589	2179.1
	e_1'	.4478	2233.1				
	e_1	.4471	2236.7		b_1'	.4574	2186.5
	e_2	.4460	2242.2	10	b_2'	.4559	2193.5
					c_1'	.4535	2204.9
					c_2'	.4520	2212.4

Rubidium Uranyl Chloride.				Cæsium Uranyl Chloride.			
Group.	Series.	λ.	$\frac{1}{\lambda} \times 10^3$.	Group.	Series.	λ.	$\frac{1}{\lambda} \times 10^3$.
	b_2	.4419	2262.7		d_1''	.4506	2219.1
	c_1	.4401	2272.0		d_2'	.4497	2223.7
	d_2'	.4362	2292.6		d_2	.4486	2229.2
11	e_1'	.4340	2304.2	10	d_2''	.4478	2233.1
	e_1	.4331	2309.0		e_2'	.4467	2238.6
	e_2	.4323	2313.2		e_2''	.4454	2245.0
					a_1'	.4445	2249.7
	b_1''	.4294	2328.8				
	c_1	.4270	2341.9		b_2'	.4419	2263.0
	c_2''	.4251	2352.4			.4412	2266.3
	d_1	.4237	2360.2		b_2	.4408	2268.6
12	d_2'	.4231	2363.3		b_3	.4398	2273.8
	e_1'	.4211	2374.7		c_1	.4388	2278.7
	e_1	.4204	2378.7		c_2'	.4380	2283.1
	e_2	.4197	2382.7		d_1''	.4364	2291.3
	a_1'	.4181	2391.5		d_2'	.4355	2296.2
				11	d_2	.4346	2300.8
	b_1''	.4164	2401.3		d_2''	.4339	2304.9
	c_1	.4147	2411.4		e_2'	.4328	2310.3
13	e_1'	.4088	2446.2		e_2	.4322	2314.0
	e_1	.4081	2450.4		e_2''	.4314	2317.8
	a_1'	.4059	2463.4		a_1'	.4306	2322.3
14	e_1'	.3972	2517.3		b_2'	.4284	2334.0
	a_1'	.3947	2533.6		c_1	.4256	2349.7
					c_2	.4243	2356.0
	b_1''	.3935	2541.0		d_2'	.4229	2364.4
	b_2''	.3922	2549.4	12	d_2	.4220	2369.4
	c_2''	.3904	2561.5		d_2''	.4205	2378.0
15	d_1	.3889	2571.4		e_2	.4196	2383.0
	d_2'	.3880	2577.3		e_2''	.4187	2388.6
	e_1'	.3865	2587.5		a_1'	.4178	2393.5
	e_2	.3849	2597.8				
					b_2'	.4159	2404.7
	b_1''	.3826	2613.4		b_2	.4149	2410.5
16	c_2''	.3796	2634.4		b_3	.4140	2415.5
					c_1	.4130	2421.3
	b_1''	.3722	2686.4	13	c_2	.4119	2427.8
	c_1	.3707	2697.6		d_1''	.4104	2436.4
	c_2''	.3695	2706.4		d_2	.4097	2440.8
					d_2''	.4090	2444.7
					b_2'	.4038	2476.3
					b_2	.4031	2480.6
				14	c_1	.4013	2491.6
					c_2	.4003	2498.1

Rubidium Uranyl Chloride.				Cæsium Uranyl Chloride.			
Group.	Series.	λ.	$\frac{1}{\lambda} \times 10^3$.	Group.	Series.	λ.	$\frac{1}{\lambda} \times 10^3$.
					d_1''	.3997	2501.9
					d_2'	.3986	2508.5
					d_2	.3979	2513.2
				14	e_2	.3960	2525.3
					e_2''	.3953	2529.7
					a_1'	.3946	2534.3
					b_2'	.3928	2545.5
					b_2	.3921	2550.4
					c_1	.3905	2560.5
				15	c_2	.3895	2567.4
					d_2'	.3877	2579.3
					d_2	.3869	2584.6
					e_2	.3854	2594.7

would permit. We are convinced, however, that the extreme limits of the absorption, in both directions, have not as yet been reached.

While this study was in progress one of the authors[1] undertook to find more absorption bands in the reversing region. As a result of this investigation several new bands were located, sufficient to extend the reversals two complete groups toward the red beginning at 5050 Å. U. These bands are excessively dim and were located only after considerable study. Where, as in many cases, they are reversals of fluorescences they are designated by capital letters.

The absorption spectra of the double chlorides do not exhibit the same remarkable approach to identity of structure and regularity of arrangement manifested in the fluorescence spectra. Upon analysis however they are all found to consist of series having intervals of approximately 70 frequency units. As may be seen from Table IX. this interval for a given series is very nearly the same for all four salts. The average interval for all the series of a given salt is constant within the errors of observation.

The absorption bands, unlike those of the fluorescence spectrum do not appear to fall into a succession of strictly homologous groups, but this is because some series disappear, while others increase in strength towards the violet. A group near the fluorescence region therefore differs notably in aspect from one in the extreme violet. It is therefore difficult to base conclusions on the location of the centers of the groups as was done in the study of the fluorescence spectra.

[1] Howes, H. L., PHYS. REV. (2), XI, p. 66, 1918.

TABLE IX.

Average Intervals of Absorption Series at + 20° C.

Series.	K.	NH_4.	Rb.	Cs.	Average.
b.....	70.5	71.6	70.4	70.9	70.9
β.....				70.6	
c.....	70.8	68.8	70.3		70.0
γ.....	70.4	70.7	70.4		70.5
d'.....				70.9	
d.....	71.1	71.0	71.2	70.3	70.9
d''.....	70.6	70.3			70.5
e.....	70.0	69.7	70.8	70.6	70.3
e''.....	70.4	70.8	69.6		70.3
a.....				70.8	
a''.....	70.0		69.3		69.7
Average....	70.5	70.4	70.3	70.6	

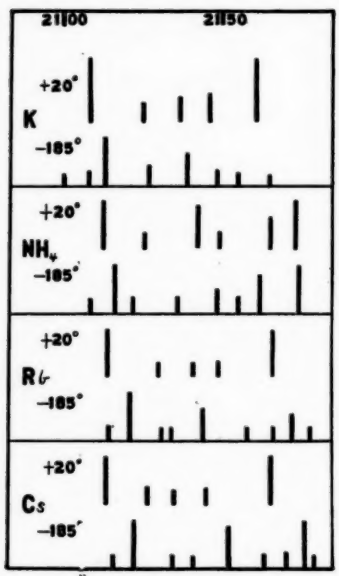

Fig. 4.

As may be observed in Fig. 4, where the ninth group for the four spectra at + 20° is plotted the distances between the consecutive bands are of the same order as the distances between fluorescence bands, as shown in Fig. 1, but are less nearly equal. It is also evident from this figure that with increasing molecular weight there is a general shift toward the violet. The shift is apparently less systematic than with the fluorescence bands and several reverse shifts seem to occur.

In the case of such bands as show a regular shift, however, the total displacement is approximately the same as that observed for fluorescence, *i. e.*, five frequency units from potassium to cæsium.

THE EFFECT OF TEMPERATURE ON ABSORPTION.

A complete list of the absorption bands which have been observed at − 185° is given in Table VIII.

In Fig. 4 the absorption bands of the ninth group at − 185° may be compared with those of the + 20° spectrum.

Two results of cooling appear: there is a general shift toward the violet and more bands are present. By the spectroscopist a third and more striking change would be noticed during the cooling process, viz., the very decided narrowing and sharpening of the bands.

These changes are readily accounted for by means of the assumption already made, in this and previous papers, that the bands at + 20° C. are concealed doublets and that the effect of cooling is to resolve them while simultaneously reducing the strength of the stronger and increasing the strength of the weaker component. The apparent shift thus produced will vary from zero to five or more units according to the distance between the components.

A few bands at − 185° are so located with regard to the + 20° bands that to explain them by this theory we must suppose them to be too feeble at + 20° for detection and greatly increased in intensity by cooling.

There is also evidence in places of further resolution into closer narrow doublets and as the degree of resolution is not always the same with fluorescence and the corresponding absorption this is a source of trouble if one attempts to find the fluorescence series which belongs to each series in the absorption spectrum. Every low temperature band, however, falls into a series of constant frequency whatever its position or degree of resolution.

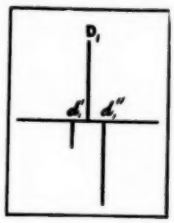

Fig. 5.

The effect of temperature on the average intervals can be studied by comparing Tables IX. and X. Although the intervals range from 69 to 71 there is little that can be termed systematic in the variations.

At liquid air where two or more components are present we have used subscripts: such as d_1, which corresponds to D_1, d_2 to D_2, etc. Where the reversal is doubled in the manner shown in Fig. 5 we have designated this doublet as d_1' and d_1'', etc.

The average interval of each salt is approximately the same at both temperatures. It will be noticed in Table IX. that 70.28, the average of the "*c*" components is smaller than the "*b*," "*d*," "*e*," or "*a*" averages. This is of interest because the strong "*C*" series, which join these series, have the shortest intervals of the fluorescence series. Since the − 185° bands are very sharp and easy to locate no doubt the differences found in Table X. are indicative of real variations in the constant frequency intervals. It does not follow that the smaller intervals are confined to one salt or one set of bands, however, since, as has been noted in the case of series C_1 and C_2 of the fluorescence series, the maximum difference in interval may be associated with two series which are nearly coincident.

The comparison of Table IX. with Table X. shows that the effect of changing temperature on the a verage interval of a salt is almost negligible but that the two components of one series of the + 20° spectrum may vary by 1.9 units in frequency interval.

TABLE X.

Average Intervals of Absorption Series at − 185° C.

	K.	NH_4.	Rb.	Cs.	Average.
b_1'.....	70.6			70.4	70.50
b_1.....		71.4			71.40
b_1''.....			71.3		71.30
b_2'.....		71.0		70.6	70.80
b_2.....	70.5		70.7	70.2	70.47
b_2''.....		71.4			71.40
b_3.....		71.2		70.7	70.95
b average...					70.83
c_1'.....				70.3	70.30
c_1.....			70.7	70.5	70.60
c_2'.....	69.3			70.9	70.10
c_2.....	70.0	70.9	70.4		70.43
c_2''.....	69.0		70.9		69.95
c average...					70.28
d_1.....	69.8		70.9		70.35
d_1''.....		70.8		70.2	70.50
d_2'.....			71.2	70.5	70.85
d_2.....	70.0			71.0	70.50
d_2''.....		70.5	71.1	70.7	70.68
d_3.....	70.2				70.20
d average...					70.51
e_1'.....			70.7		70.70
e_1.....	70.6	70.7	70.9		70.73
e_2'.....	70.5			70.0	70.25
e_2.....			70.8	70.3	70.55
e_2''.....		71.4		70.8	71.10
e average...					70.67
a_1'.....			71.0	71.0	71.00
a_1.....	70.0	71.3			70.65
a_2.....	70.4		70.4	70.6	70.47
a_2''.....	71.9				71.90
a average...					71.00
Average....	70.22	71.06	70.84	70.54	

REVERSALS AND THE REVERSING REGION.

The early observers of uranyl spectra were of the opinion that some connection or relation must exist between the system of bands of fluorescence and absorption. Becquerel and Onnes who first studied these spectra at low temperatures, were able to confirm the impression of Stokes that the two systems overlapped and that there was actual coincidence of position between certain fluorescence bands and absorption bands.

In the case of the double chlorides at + 20° each series of bands of the fluorescence system comes into coincidence, or near coincidence with an absorption band in what we have termed the reversing region, which is approximately that region occupied by group 7 of the fluorescence spectrum.

The fact that the reversal sometimes appears to be exact, within the errors of observation, while sometimes there is a displacement of several units of frequency might seem to render such a general relation doubtful, but the discrepancy can be shown to be a necessary consequence of the fact that both fluorescence and absorption bands at this temperature are unresolved complexes. The true nature of the case may be seen from Fig. 6 which is from a sketch of such a reversal at − 185° where the resolution is more nearly complete. Here the fluorescence and absorption are complementary, the strong component of fluorescence coinciding with the weak absorption component and vice versa. When the resolution is less complete the weaker components will disappear and although the reversal for each component is exact there will be an apparent failure to reverse, or in other words we see the strong components displaced.

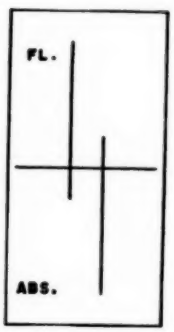

Fig. 6.

In the reversing region fluorescence and absorption are mutually destructive. Consequently one or both are sometimes invisible; but knowing the intervals we can locate the reversal. By proper screening the fluorescence may be prevented and the absorption band brought out; and by taking extra precautions to secure a dark back ground and to increase the excitation the fluorescence may be seen. Thus the computation may be confirmed.

In the study of the double chlorides the matter is further confused because the difference between the fluorescence interval (83.+) and that of the absorption interval (70+) is approximately equal to the distance between neighboring bands in the fluorescence groups. An absorption series which comes into coincidence with band *C*, group 7 will therefore

nearly coincide with band *B*, group 8, etc. Furthermore the degree of resolution in the absorption spectrum as has already been mentioned is often greater than in the fluorescence spectrum and certain series are observable of which the corresponding fluorescence bands cannot be identified.

So far as the spectra at + 20° are concerned, we find that:

1. All absorption bands towards the violet from the reversing region occur in series with constant frequency intervals.

2. For every fluorescence series there is a corresponding absorption series.

Whether the relation between absorption and fluorescence outlined above is significant can best be determined by the study of the spectra for − 185°.

If for example the explanation of the numerous instances of inexact coincidence is valid we should expect exact reversals of the components; also that the components of the resolved absorption spectra form series definitely related to the components of the fluorescence spectra in a manner consistent with the system indicated for the spectra at + 20°. From a study of the exactness of the reversals in the resolved spectra at low temperatures it appears that twenty-five out of thirty-eight fluorescence series are certainly reversed and that thirty-six fluorescence series join absorption series in the seventh group. The experimental error in this group does not exceed 1.5 units. The difference in position between fluorescence and absorption is sometimes greater than 1.5 but this may be ascribed to the dissymetry in the form of the bands.

Fluorescence bands have their crest towards the violet, absorption bands towards the red. In the case of reversals, these regions tend to annul each other, leaving a remnant of fluorescence on the red side and a remnant of absorption on the violet. The result is that in regions where fluorescence and absorption exist together, fluorescence bands are apt to be given too great a wave-length and vice versa. In the C_2 series of the rubidium chloride, for example, there is a displacement of 2.6 units between the *observed* positions of fluorescence and absorption.

If however we compute the proper positions of these bands using the average intervals for the C_2 and c_2 series respectively, thus eliminating the displacements in the reversal region, the fluorescence band and absorption thus established agree in position within 0.3 unit. The impossibility of excluding all absorption when fluorescence is present, and vice versa, the impossibility of preventing a tendency towards fluorescence when absorption alone is sought for may well account for the resulting displacement. The case of the C_2 series is not an isolated

one—probably every reversal is affected somewhat and the stronger bands the most; there being always an apparent shift of the absorption band towards the violet and of the fluorescence band toward the red. This phenomenon has long been recognized by the authors in connection with the broad fluorescence bands and it must now be recognized in the reversing of the narrow, line-like bands at the temperature of liquid air.

In the above, the reversals which connect fluorescence to absorption series have been sought for in the seventh group. There are however other possible connections, for coincidences occur in the sixth and eighth groups as well. Since, as has already been pointed out, the difference in

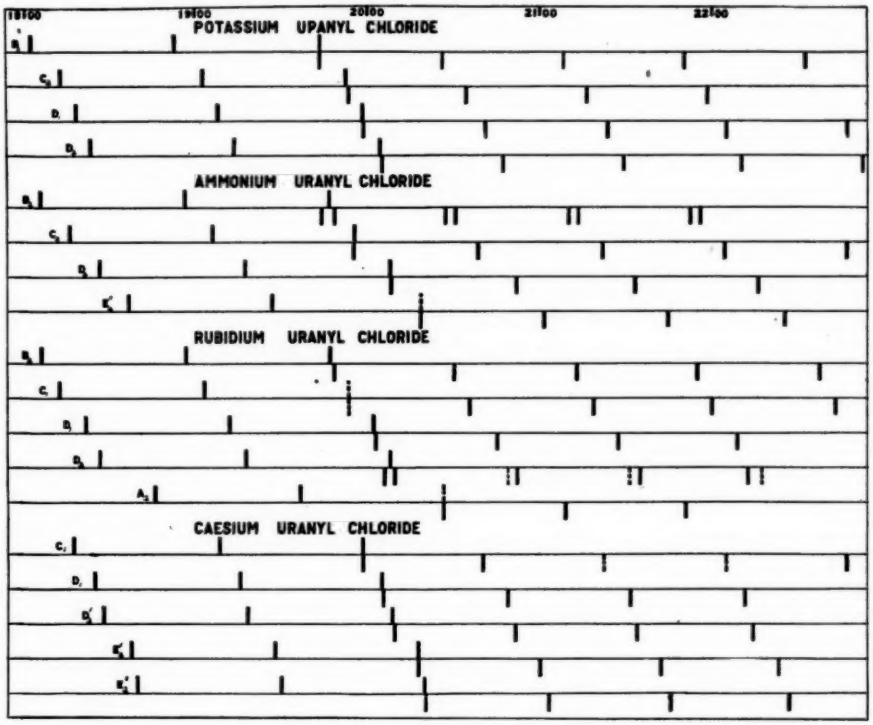

Fig. 7.

spacing between a fluorescence and absorption interval is nearly the same as the spacing between fluorescence bands it is often possible to join equally well two fluorescence series to one absorption series; a fact which makes it difficult to determine the true relation in the case of this class of salts.

The actual manner in which the reversals between fluorescence and absorption occur is shown in Fig. 7, which is a diagram of the reversing region. Here the plotting is quite accurate, the fluorescence bands above

and the absorption bands below the horizontal. Dotted lines indicate computed positions. This cut is approximately ten times as large as the original negatives. To avoid confusion the various series occurring in each salt are vertically displaced instead of being drawn on a single line, as they appear in the actual spectra. An inspection of this diagram will suffice to indicate the approach to complete coincidence in the reversals and the type of departure from coincidence.

With regard to the reversing region at $-185°$ it can be stated that

1. The majority of the fluorescence series reverse in the seventh group.

2. Thirty-six out of thirty-eight fluorescence series are joined in the seventh group to absorption series.

3. The exactness of reversal depends not only on the structure of the band but on the simultaneous presence of fluorescence and absorption in this region.

4. Other reversals and connections are present in the groups adjacent to group seven.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY,
October 10, 1917.

YOUNG'S MODULUS OF DRAWN TUNGSTEN AND ITS VARIATION WITH CHANGE OF TEMPERATURE, INCLUDING A DETERMINATION OF THE COEFFICIENT OF EXPANSION.

BY H. L. DODGE.

THIS paper is the fourth of a series upon the effect of temperature upon the elasticity of wires and deals with tungsten. The method is the same, in general, as that employed in previous work with copper,[1] mild steel,[2] and aluminum[3] wires, but the apparatus has been entirely rebuilt and embodies a number of improvements. In the present form it permits of the measurement of Young's modulus up to a temperature of about 800° C. with external heating and with internal heating to still higher temperatures.

OPEN TUBULAR FURNACE APPROXIMATING A BLACK BODY.

The most important improvement has been in the new furnace, which is entirely different in construction and principle from the one formerly used. The old furnace consisted of a long rectangular box of asbestos board with a glass top. The heating element lay on the bottom. Thus there was a large temperature gradient in the space around the wire and, although every precaution was taken to insure that the thermo-couples should give the temperature of the wire, there was always some error, the possible magnitude of which could be estimated only roughly.

The new furnace is constructed of a series of three coaxial tubes, each thirty inches long. The inner tube is of copper and has an inside diameter of five eighths of an inch and a one eighth-inch wall. Next comes an alundum tube wound with a heating element of nichrome ribbon. Surrounding this is an outside covering of vitribestos. In the top and in the side, 10 cm. from each end, are holes extending through all the tubes. Above the vertical holes are placed two stereopticon lamps for illumination; the wire is viewed through the horizontal holes. All the holes have mica windows.

As the loss of heat from the furnace is very much greater at the ends

[1] PHYS. REV., 2, 2, 431, 1913.
[2] PHYS. REV., 2, 5, 373, 1915.
[3] PHYS. REV., 2, 6, 312, 1915.

than at the center it is necessary to find by trial the best distribution of the heater winding to secure the most uniform temperature throughout the length of the inner tube. The latter, being of heavy copper, smoothes out all local irregularities in temperature.

In a furnace of this kind advantage can be taken of the fact that, except at the ends, the interior of a long tube which is at a uniform temperature is equivalent to a black body.[1] Even though there is an appreciable temperature gradient along the tube it is safe to assume that the temperature over any given cross-section is uniform and the same as that of the wall of the tube at that point. It is also true that every point on a wire suspended in the tube will take up a temperature almost exactly that of the cross-section in which it happens to fall. Therefore, in order to determine the temperature of a certain point on the wire, it is not necessary to place the thermo-couple in contact with the wire but merely to determine the temperature at any point situated in the same cross-section.

However, when the heating is by an electric current in the wire itself this method cannot be followed nor can thermo-couples be applied directly to the wire. It has been found that the most satisfactory method is one depending upon thermal expansion. The coefficient of expansion of the wire having been determined once for all, the same observations of length necessary for the measurement of the modulus also determine the temperature. The expansion coefficient is found by the following method.

MEASUREMENT OF THE COEFFICIENT OF THERMAL EXPANSION.

A certain current is passed through the heating element and allowed to flow for a definite time, let us say one hour. During the last few minutes the current is kept very steady by means of a potentiometer. At exactly the end of the hour the electromotive force of a thermo-couple, inserted to the middle of the furnace, is read. A larger current is then passed for a definite time, known to be sufficiently long for the furnace to reach a condition of equilibrium. Readings of the heating current and of the thermo-couple E.M.F. are again taken. This process is repeated until the highest temperature permitted by both furnace and wire is reached.

After the furnace has cooled the thermo-couple is removed and the wire suspended in the furnace. Then exactly the same procedure as before is followed, except that the thermo-couple readings are replaced by measurements of the change of length of the wire. Thus for every

[1] Analogous to the uniform field of a long solenoid.

thermo-couple reading there is a corresponding measurement of the increase of length of the wire, made under identically the same conditions of temperature. From these observations the coefficient of thermal expansion can be readily computed.

The variation of temperature along the tube was investigated in order that the average temperature of the wire over the portion under observation could be found from the temperature measured. When the center of the furnace was at 673° C. at no point between the centers of the windows did the temperature differ from this value by as much as five degrees.

THE TESTS.

The tests were made upon a piece of drawn tungsten wire secured through the kindness of Dr. A. G. Worthing, of the Nela Research Laboratory. The wire was obtained in December, 1914, and was said to contain approximately 99 per cent. tungsten and one per cent. thorium. It has a diameter of 0.65 mm.; the length under observation was 593.6 mm. The thermal expansion was found to be practically uniform over the temperature range covered, namely 20° C. to 675° C., the coefficient of expansion being .00000456 per degree Centigrade. This value checks exactly, for the temperature range covered, with that of Worthing[1] but

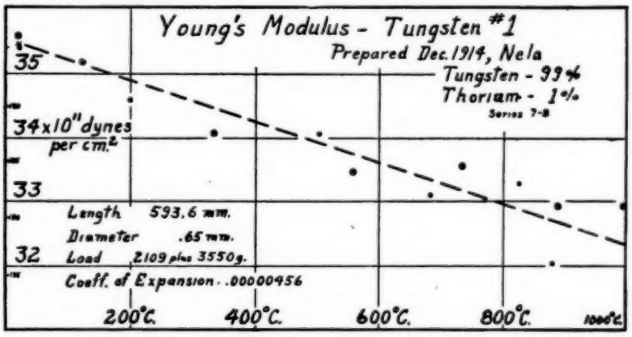

Fig. 1.

Effect of temperature upon the Young's modulus of drawn tungsten.

does not verify that of Langmuir,[2] from which it differs by as much as fifty per cent. Worthing's formula was used in determining temperatures above 675° C.

In measuring the modulus of elasticity the permanent load was 2,109 g., the added load, 3,550 g. The Young's modulus of drawn tungsten was found to be 35.5×10^{11} dynes per cm.² at 20° C. This value is

[1] Jour. Frank. Inst., 181, 857, 1916; PHYS. REV., 2, 10, 638, 1917.

[2] PHYS. REV., 2, 7, 329, 1916.

undoubtedly accurate to within two or perhaps three per cent. This is somewhat lower than the value given by Fink[1] of 42,200 kg. per sq. mm., but it is entirely possible that there is that much difference in the modulus of wires prepared at different places and at different times, for the art of drawing tungsten wires has had a recent and rapid development.

The change of the modulus with increase of temperature was observed up to 1,000° C. at which temperature the oxidation of the wire became very rapid. However it was possible to check back after readings at about 900° C., as shown in Fig. 1. The dots represent observations taken with increasing temperature, the last at 880° C. The cross is the value found immediately after the wire had cooled. The dotted circles represent the next series of readings.

Only two series of readings are shown in the figure. These were preceded by a great deal of preliminary work, necessary to determine the magnitude and general nature of the effect of temperature and to learn what loading should be used. On account of the extremely high value

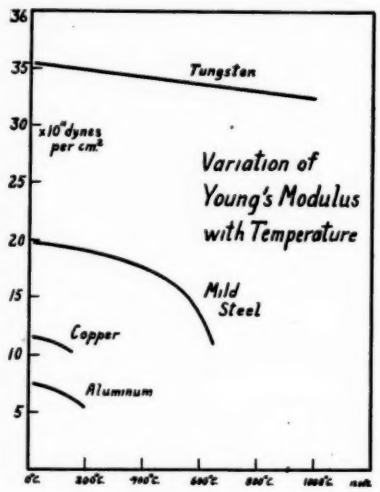

Fig. 2.

Comparative effects of temperature upon the Young's modulus of aluminum, copper, mild steel and tungsten wires.

of the modulus much heavier weights than usual were necessary. Even with a load of over 3.5 kg. the *variation in the stretch over the whole temperature range amounted to but eighteen thousandths of a millimeter.* The actual stretch in thousandths of a millimeter corresponding to the different values of the modulus is indicated at the left edge of Fig. 1.

All of the observations were taken when the heating was by a current

[1] Trans. Am. Electrochem. Soc., 22, 503, 1912.

in the wire itself as it was found that the manner of heating did not affect the results and this method was the more convenient.

A temperature of 1,000° C. is so low in comparison with the melting point of tungsten that one could hardly expect it to show the characteristics of the other metals with lower melting points. However there is nothing in the behavior of tungsten which is not in harmony with the general conclusions already reached regarding the effect of increase of temperature upon elasticity.[1] In Fig. 2 the effects with tungsten and with the three other metals are compared.

SUMMARY.

The Young's modulus of drawn tungsten is 35.5×10^{11} dynes per cm.^{2} at 20° C. The modulus decreases uniformly with increase of temperature up to 1,000° C. at which temperature it is 32.3×10^{11} dynes per cm.^{2}

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[1] Dodge, PHYS. REV., *2*, 6, 316, 1915.

A NEW METHOD OF POSITIVE RAY ANALYSIS.

BY A. J. DEMPSTER.

THE analysis of positive rays is based on the determination of the ratio of the charge to the mass of various constituents. The corresponding measurement for the negative corpuscle has however been carried to a much greater degree of accuracy by means of methods involving the magnetic deflection of the rays through large angles, and the refocusing of rays which make slightly varying angles with each other. Apart from the accuracy of the measurement, there is also in these methods a great resolution between slightly different speeds; thus Rutherford and Robinson[1] have separated distinct groups of β rays from RaC which differ by 2 per cent. in energy; also the photographs given by Classen[2] for electrons show such sharpness that if electrons had masses differing by as little as 1 in 100, the various groups would be separated. With positive rays the slit method used by Richardson[3] is suitable for weak sources and allows a fairly exact measurement of a mean molecular weight, but the curves given in the above paper show that the power of separating different elements is very small. The method used by J. J. Thomson is capable of comparatively great resolving power, elements being sharply separated which differ in molecular weight by 1 in 16,[4] but this is obtained only with a great loss in intensity. The method developed in the present experiments was expected to give great intensity with moderate resolution. It was found that the method could also be developed to give a very great resolving power among the elements.

The method is essentially identical with that used by Classen in his determination of e/m for electrons. The charged particles from some source fall through a definite potential difference. A narrow bundle is separated out by a slit and is bent into a semicircle by a strong magnetic field; the rays then pass through a second slit and fall on a plate connected to an electrometer. The potential difference (P.D.), magnetic field

[1] Phil., May 26, p. 725, 1913.

[2] Jahrb. d. Hamburg Wiss. Anst., Beiheft, 1907.

[3] Phil., May 16, p. 757, 1908; The Emission of Electricity from Hot Bodies, p. 196.

[4] Nature, 86, p. 468, 1911.

(H_0), and radius of curvature (r) determine the ratio of the charge to the mass of the particles by the usual formula

$$\frac{e}{m} = \frac{2 \cdot PD}{H_0^2 r^2}.$$

The apparatus consisted of the glass tube G, where the positive particles fell through a definite potential difference, and the analyzing chamber A, in which a strong magnetic field was produced between two semicircular iron plates 2.8 cm. thick and 13 cm. in diameter. The iron plates were soldered into half of a heavy brass tube B so as to leave a passage or slot 4 mm. wide between the plates. A plate of brass on top C closed this slot except for three openings into which short brass tubes were soldered. The glass tube G fitted into the first opening and a tube for exhausting into the second. The electrometer connection passed to a receiving plate through an ebonite plug E which formed a ground conical joint with the third brass tube. The two openings for the rays had adjustable slits S_1, S_2, and a screen D was introduced into the analyzing chamber to prevent reflected rays getting into the second slit. The whole was placed between the poles of a powerful electromagnet. The strength of the magnetic field and the manner in which it fell off above the entrance was determined with a test coil. The throws obtained on removing the coil rapidly were compared with the throws obtained from two coils whose mutual inductance was known, when the current through one was broken. In this way a curve was drawn connecting the field strength and the current through the electromagnet. The current was always reversed slowly several times before taking a reading. The field strength was the same over the whole area of the plates to within one per cent. The rays were obtained either by heating salts on platinum strips, as in Richardson's experiments, or by bombarding salts with electrons; in the latter case the salts were either heated by the bombardment or were heated independently while being bombarded.

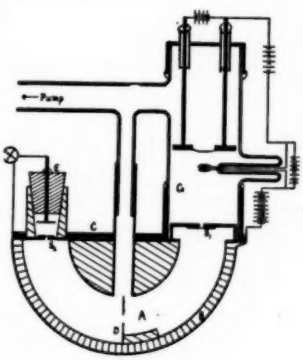

Fig. 1.

It might be thought from the elaborate precautions taken in the experiments by Wien and Thompson to prevent the discharge tube being influenced by the magnetic field used for deflecting the rays, that great difficulty would be experienced in introducing the rays properly into a sufficiently strong magnetic field, and in drawing conclusions from

the deflection observed. But such is not the case. The equations for the motion of a charged particle in a longitudinal electric field (PD/a) parallel to the z-axis, and a transverse magnetic field $H(z)$ parallel to the x-axis are

$$\frac{d^2z}{dt^2} = \frac{e}{m} \cdot \frac{PD}{a}; \qquad \frac{d^2y}{dt^2} = \frac{e}{m} H \frac{dz}{dt}.$$

The integration of the first gives

$$\frac{dz}{dt} = \sqrt{\frac{2e \cdot PD}{m \cdot a}}\, z^{1/2},$$

and using this in the second we get on integrating

$$\frac{dy}{dz} = \sqrt{\frac{e}{m} \cdot \frac{a}{2PD}}\, z^{-1/2} \int_0^z H(z)dz.$$

$$\therefore \quad \left(\frac{dy}{dz}\right)_a = \sqrt{\frac{e}{m} \frac{1}{2PD}} \cdot \int_0^a H(z)dz = \frac{1}{rH_0} \int_0^a H(z)dz. \qquad (1)$$

If we put

$$z^{-1/2} \int_0^z H(z)dz = K(z)$$

$$y_a = \frac{a}{H_0 r} \int_0^a K(z)dz.$$

(1) also applies to the case of particles moving in a magnetic field alone. The magnetic field was reduced to zero at the place of origin of the rays by the use of a secondary electromagnet, and the values of the above integrals were observed and calculated by means of a coil wound on a long rectangular frame. If the first slit were placed directly at the entrance to the 4 mm. slot, it was found that the rays would be deflected a distance $y_a = .96$ mm. and through an angle whose tangent $(dy/dz)_a = 1/9.3$. This might be sufficient to destroy the refocusing and to make uncertain the value of r in the equation

$$\frac{m}{e} = \frac{H_0^2 r^2}{2 \cdot PD}.$$

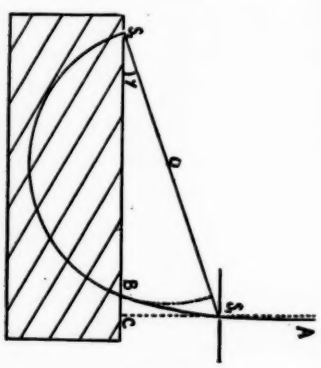

Fig. 2.

These difficulties may however be completely avoided by the simple device of moving the entrance slit out in front of the iron plates. Let the shaded portion in Fig. 2 represent the iron plates, and S_1S_2 the two slits where the distance S_1B is much exaggerated. The geometrical

condition for refocusing is that S_1OS_2 should lie on a straight line. We therefore wish that the figure as drawn should apply to the rays. For this we must have $\gamma = \alpha + \beta$, where α = angle of deflection in AS_1 and β = angle of deflection in S_1B. That is, if $S_1C = b$,

$$\frac{b}{2r} = \frac{1}{H_0 r}\int_A^{S_1} H(z)dz + \frac{1}{H_0 r}\int_{S_1}^{B} H(z)dz$$

or

$$b = \frac{2}{H_0}\int_A^B H(z)dz.$$

This value was calculated to be .93 cm. and the slit S_1 was placed at that distance in front of the iron plates. The distance BC was calculated to be .25 mm. The correct radius of curvature is very closely $(S_1S_2 - BC)/2$ to which $(S_1S_2)/2$ is a sufficient approximation. A high vacuum was obtained by a mercury vapor pump, which acted in connection with a Gaede rotary mercury pump. Mercury vapor must be kept away from the apparatus at all times by the use of liquid air, for in a very short time sufficient will diffuse over and condense on the brass to prevent a high vacuum being obtained.

If the charged particles all fall through the same potential difference, the most reliable method for analyzing the rays is to keep the magnetic field constant, and vary the potential difference so as to bring successive elements onto the slit, for in the fundamental equation and in (1), m and PD occur only in the product $m \cdot PD$, and the rays will therefore follow identical paths for $m \cdot PD$ = const. This would allow the comparison of molecular weights with the accuracy of a potential measurement; and if a molecular weight is known the original magnetic field determinations can be corrected. If, however, charged surface layers are formed on the salts from which the ions start, the above method would not be reliable. It was found that in practically all cases the calculated molecular weights came out very close to the chemical molecular weights, so that no assumptions of surface layers comparable to the potentials used, and only small corrections to the magnetic field determinations were necessary. An exception occurred with very weak magnetic fields, but this is at present ascribed to the difficulty in reproducing the magnetic fields with very weak currents.

Resolving Power.

If the rays were uniformly distributed over the entrance slit and the refocusing perfect, the curve obtained for the charge as the potential or field strength is varied to bring various parts of the bundle on the exit slit, would be of the form given in Fig. 3. Let S be the width of the slits

and h_1h_2 represent the abscissæ where the curve is half its maximum value. $S = h_1h_2$ if the abscissæ represent distances. In order to see what change in m is necessary to produce a displacement h_1h_2, we have from the formula

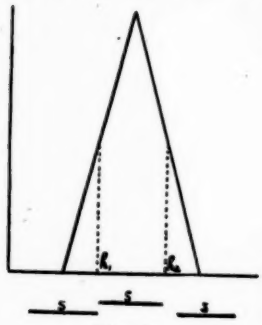

Fig. 3.

$$m = \frac{eH_0^2r^2}{2 \cdot PD}$$

$$\frac{\Delta m}{m} = \frac{2\Delta r}{r} = \frac{2\Delta d}{d} = \frac{2S}{d},$$

where $d = 2r$. This may be called the limit of resolution, and if two molecular weights differ by this amount, the point h_1 of the one coincides with the point h_2 of the other. In the apparatus $d = 10$ cm., so that for slits $\frac{1}{2}$ mm. wide we should have

$$\frac{\Delta m}{m} = \frac{1}{100}.$$

Preliminary Experiments.

The first experiments were made with ions obtained by heating a mixture of sodium phosphate and calcium oxide on a platinum strip. Several widely separated groups of rays were observed with slits about 2 mm. wide. The molecular weights agreed approximately with Na and K for the strongest positive, and with O_2 and CaO for the strongest negative lines. The positive emission changed gradually with heating, from being entirely potassium to being mostly sodium.

In another experiment manganous chloride ($MnCl_2$) was heated and the negative emission was observed. Three distinct molecular weights were observed which agreed approximately with negatively charged oxygen molecules, manganese with a double negative charge, and manganous oxide with a single charge.

Positive Ions from Aluminium Phosphate.

The positive ions obtained from heated aluminium phosphate have been used by many experimenters. These ions were analyzed and found to consist usually of sodium and potassium, although on one occasion after standing overnight, the emission was at first entirely hydrogen atoms. This wore off in a few minutes and the emission became sodium and potassium. At first the potassium was very much stronger than the sodium, but after heating some time it died off and became much weaker. The emission was examined only at low temperatures as with increasing temperature the currents soon became inconveniently large.

TABLE I.

P.D.	*M.*	Current.	P.D.	*M.*	Current.
679	22.79	3.8	705	21.93	117.
685	22.57	17.8	711	21.74	80.
689	22.44	43.5	715	21.62	58.8
693	22.31	90.9	719	21.50	20.8
699	22.12	133	723	21.39	3.3

As an example the figures in Table I. give the actual readings in one measurement of the sodium line. The entrance slit was 1.9 mm. wide, the exit slit 1.65 mm. wide and a screen 3.3 mm. wide was placed half way around the semicircle. The current through the electromagnet was kept constant at .8 ampere giving a magnetic field of 3,580 gausses according to the curve drawn from the original determinations. The potential difference (*PD*) which was obtained from banks of small storage cells is given in volts, and the molecular weight $M = m/m_1$, is calculated from

$$m = \frac{eH^2_0r^2}{2V}$$

and

$$m_1 = \frac{e}{9650}\ ;\ r = 5 \text{ cm.}, e = 1{,}591 \times 10^{-20}.$$

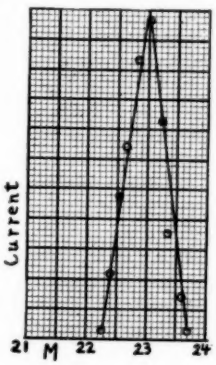

Fig. 4.

The current given was observed with the electrometer for the different potentials between the heated salt and the slit. The maximum comes at 22.1, but, as there can be no doubt that this line really is sodium, we can explain the difference as due to the value of the magnetic field being 2 per cent. too low. The difference is probably not due to the ions falling through less potential difference than the total applied, since, with other values of the magnetic field, values of M very close to 23 were obtained. The curve, Fig. 4, is drawn with the magnetic field corrected to bring the maximum at 23, and shows an approximation to the theoretical form of Fig. 3. The limit of resolution should be between

$$\frac{\Delta m}{m} = \frac{2 \times 1.65}{100} = .033$$

and

$$\frac{2 \times 1.9}{100} = .038,$$

whereas that observed is $.7/23 = .028$. The form of the curve shows that the influence of the small amount of gas remaining is very slight.

Fig. 5 gives the curves for sodium and potassium under slightly poorer vacuum conditions, both taken while the magnetic field was held constant at 5,200 gauss. The maximum for sodium was obtained with 1,433 volts and for potassium with 845 volts. The ratio is almost exactly 39 to 23. The curve is drawn with a slightly corrected magnetic field so as to bring the sodium maximum from 22.8 to 23.00. The potassium ordinates are multiplied by 50 so that the sodium in this case was about 90 times as strong as the potassium. These curves indicate that the charged particles actually fall through the total potential difference.

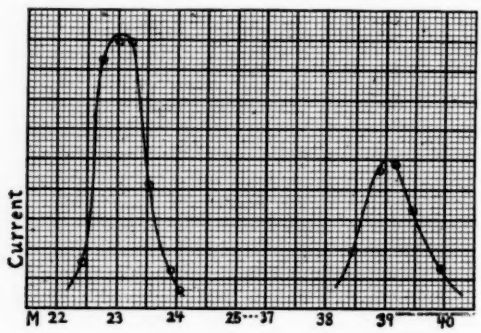

Fig. 5.

The emission starts rather suddenly as the temperature of the strip is raised, in the manner discussed by Richardson; but it was observed that the potassium emission commences at a lower temperature than the sodium. As the temperature was lowered the sodium disappeared while the potassium was still strong. The Table II. gives the currents observed

TABLE II.

K.	Na.
1.9	0
38.4	1.4
62.5	5
71.4	19
208	91
52.6	2000

for each as the temperature was raised by increasing the heating current. The potassium is much stronger than the sodium at first but at higher temperatures the sodium becomes the stronger.

No great difficulty is expected in extending the investigation to all the substances found by Richardson and others to emit positive or negative ions on being heated. With weak sources it will be necessary to widen the slits and be content with less resolution.

Positive Ions from Electron Bombardment.

It was thought that the bombardment of salts by electrons might break up the chemical compounds and give rise to many positive ions. At first a Wehnelt cathode was used; the ions formed passed beside the cathode (Fig. 1) and were then accelerated by a large potential difference. Aluminium phosphate on a piece of platinum foil was first bombarded. The intensity of the rays increased very rapidly with a slight increase in the amount or energy of the bombarding electrons, indicating that the salt needs to be heated to a certain degree before the ions are separated. Although the aluminium phosphate was chemically pure, the rays obtained under the bombardment of 128 volt electrons were very complex; the following ions were observed besides a couple of unresolved groups; H_1, H_2, Li (weak), O_1 (strong), Na (strong), O_3 (?) (weak), $M = 62$ (weak, possibly Na_2O), $M = 67$ (strong, possibly $H_3PO_2 = 66$), $M = 76$ (strong), $M = 86$ (weak, possibly Rb = 85.5), $M = 112$ (strong, possibly $P_2O_3 = 110$).

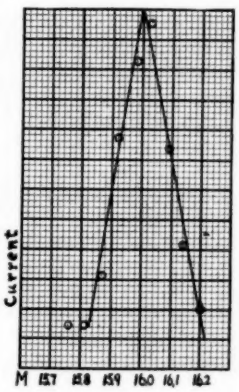

Fig. 6.

The experiments indicated the convenience of the method of obtaining positive rays and opened up an interesting field for investigation.

The experiments were however first directed towards testing out the possibility of obtaining still greater resolving power. The curve in Fig. 6 for oxygen from the bombardment of aluminium phosphate was obtained with $\frac{1}{2}$ mm. slits and two screens with 2 mm. openings placed in the path of the rays. Table III. gives the actual observations. The magnetic field has been corrected so as to bring the maximum from 16.73 to 16. The theoretical resolution is

Table III.

P.D.	*M.*	Current.	P.D.	*M.*	Current.
1,758	15.76	7.3	1,728	16.03	58
1,752	15.81	7.3	1,722	16.09	37
1,746	15.87	15.6	1,716	16.14	21
1,740	15.92	38.6	1,710	16.20	10
1,734	15.98	51			

$$\frac{\Delta m}{m} = \frac{2 \times .5}{100} = .01;$$

the observed is .2/16 = .012. From the bombardment of aluminium phosphate to which a little lithium chloride and sodium chloride had been added strong bundles of hydrogen atoms and hydrogen molecules were obtained. With slits ½ mm. in width and a screen with an opening 4 mm. in width placed in the path of the rays, the curves in Fig. 7 were

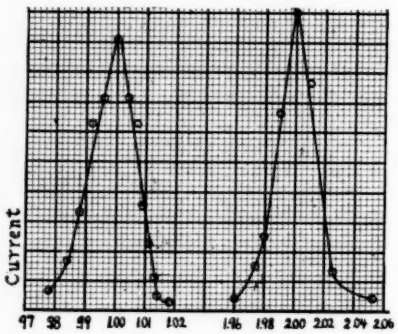

Fig. 7.

obtained. The magnetic field has been corrected to shift the maximum from .92 to 1.00 and from 1.77 to 2.00. The actual observations for the first curve are given in Table 4. The limits of resolution observed are .015 and .017.

It is generally assumed that the hydrogen and oxygen atoms are perfectly homogeneous so that the object in developing the above resolving power was to apply it to elements whose homogeneity has recently been considered a questionable matter. In a recent lecture Professor Soddy says[1]:

TABLE IV.

Volts.	*M.*	Current.	Volts.	*M.*	Current.
1,470	1.018	2.8	1,496	1.000	91
1,478	1.013	11.1	1,502	.9961	71.4
1,480	1.011	22.2	1,508	.9922	62.5
1,482	1.009	35.7	1,514	.9883	33.4
1,486	1.006	62.5	1,520	.9845	16.7
1,490	1.004	71.4	1,530	.9780	6.7

"When, among the light elements, we come across a clear case of large departure from an integral value, such as magnesium 24.32 and chlorine 35.46, we may reasonably suspect the elements to be a mixture of isotopes." With the resolving power in the above examples this question can obviously be definitely decided, for, if the element is really homo-

[1] Nature, 1917 also Scientific Monthly, p. 516, Dec. 1917. See also Fajans, Phys. Zeit., 1916.

geneous, the curve will lie entirely between two integral values, and if it is a mixture of elements differing by integers, the molecules will be completely separated. The only experimental difficulty is to get the rays, and this is the matter now under investigation. Magnesium has been tried by bombarding it with electrons from a tungsten filament while it was being heated by a platinum strip around which it was wrapped. With slits 1.9 mm. and 1.65 mm. in width intense rays of oxygen molecules (calculated 32.01) were obtained and after heating for some time rays of nitrogen or carbon monoxide (28.00) appeared. Rays that are probably chlorine have been obtained from the bombardment of a heated anode of aluminium phosphate, potassium chloride and potassium iodide with electrons from a tungsten filament. The apparatus was however at the time slightly contaminated with mercury, and the curves were so broadened that no conclusion could be drawn. A crystal of KI was bombarded and found to give strong H_1 and H_2 rays; no H_3 or helium was observed.

The experiments described above are concerned chiefly with the development of the method, and they are published now only because the writer expects to be engaged in other duties for some time.

The writer wishes to express his appreciation of the kindness of Professor Michelson and Professor Millikan in placing the equipment of the laboratory at his disposal and in rendering every possible assistance.

Summary.

An apparatus for analyzing positively or negatively charged particles is described. Examples are given of the analysis of the ions from heated salts and of the positive rays obtained by bombarding various substances with electrons. The high resolving power obtainable with the method is also illustrated.

Ryerson Physical Laboratory,
Chicago,
October 20, 1917.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE NINETY-FIRST MEETING.

THE ninety-first meeting of the American Physical Society was held in the Ryerson Laboratory of the University of Chicago on Saturday, December 1. Morning and afternoon sessions were held.

The following papers were presented:

Vacuum Gauges of the Radiometer type. R. G. SHERWOOD.

Further Verification of Knudsen's Equations for Resistance to Molecular Flow. L. E. DODD. (By title.)

A Megaphone with a Rectangular Aperture. F. R. WATSON.

The Forces Which Hold Liquids and Solids Together. WILLIAM D. HARKINS.

Rectification of Alternating Current by the Corona. J. W. DAVIS.

The Determination of Organic Compounds by an Optical Method. THOS. E. DOUBT, AND B. B. FREUD.

The Analysis of Polarized Light Reflected from Small Opaque Crystals. LEROY D. WELD.

Resonance and Ionization Potentials for Electrons in Cadmium, Zinc, and Potassium Vapors. JOHN T. TATE AND PAUL D. FOOTE.

A New Method of Positive Ray Analysis. A. J. DEMPSTER. (By title.)

Mobility of Ions in Air, Hydrogen, and Nitrogen. KIA-LOK YEN.

A Correction in the Theory of Ionization by Collision. JACOB KUNZ.

Wave Lengths of the Tungsten X-Ray Spectrum. ELMER DERSHEM.

A Mono-Wave-length X-Ray Concentrator. ELMER DERSHEM.

The Crystal Structure of Ice. ANCEL ST. JOHN.

Characteristic Curves of Various Types of Audions. A. D. COLE.

The Angle of Contact between Liquids and Glass, and the Determination of Surface Tension. WILLIAM D. HARKINS.

The Absorption and Solubility of Long-Chain Molecules. WILLIAM D. HARKINS.[2]

A. D. COLE, *Sec.*

Note on a Phosphorescent Calcite.[1]

By E. L. Nichols and H. L. Howes.

A SPECIMEN of calcite from Franklin Furnace, N. J., showing the usual red-yellow phosphorescence of short duration was studied. The after glow falls to 1/660 of its initial brightness within 0.5 second. The decay is remarkably slow at first following the usual law $I^{-1/2} : t$.

After about .16 sec., for the excitation employed, a second "linear" process begins of more rapid decay and at .30 sec. from the close of excitation this is followed by a third "linear" process of still more rapid decay. The law of decay therefore is that recently described by the authors[2] and supposed to be peculiar to the uranyl salts. Detailed spectrophotometric observations show that what appears to be a single broad band extending from .66 μ to .54 μ, is a complex of narrow overlapping bands as in the case of the spectra of the phosphorescent sulphides.[3] A second very feeble band lies between .52 μ and .50 μ with its crest at about .514 μ.

Cornell University,
December, 1917.

The Visibility of Radiation in the Blue End of the Visible Spectrum.[1]

By L. W. Hartman.

IN investigations of this type, two general methods have been utilized: (1) the direct comparison method in which the luminosity of light of successive wave-lengths emitted by the source is compared directly with that of light emitted by a second source considered as a standard, and (2) the flicker method in which the criterion of equality is the disappearance of flicker.

The first method was utilized in this paper and had been used previously in another investigation[4] in this laboratory. It consisted primarily of an adaptation of the arrangement of the parts of the Holborn-Kurlbaum optical pyrometer. One advantage of this method is that it permits the use of greater brightness so that measurements in the extreme regions of the spectrum can be made. In order to secure sufficient brightness in the extreme blue end of the spectrum, a bright, high temperature source was selected, viz., a tungsten lamp with broad vertical flat filament maintained at a color temperature[5] of 2695° K. A magnified image of this flat filament was projected on the collimator slit of a Hilger constant deviation spectrometer. Upon passing through the prism, the light from this source formed a spectrum in the focal plane of the telescope of the spectrometer where the horizontal filament of a small tungsten

[1] Abstract of a paper presented at the meeting of the American Physical Society held in Pittsburgh, December 27–29, 1917.

[2] Nichols and Howes, Physical Review (2), IX., p. 292.

[3] Nichols, Am. Philos. Soc. Proc., LVI., p. 258.

[4] Hyde and Forsythe, Astrophys. Jour., 42, p. 285, 1915.

[5] Hyde, Cady and Forsythe, Phys. Rev. (2), 10, p. 395, 1917.

pyrometer lamp served as a comparison source. A lens, in turn, placed between this comparison source and the eyepiece of the instrument, focused an image of the incandescent filament of this small lamp together with the spectrum of the source on a narrow adjustable slit placed in the focal plane of the eyepiece. In front of the eyepiece was mounted a blue glass screen. The visual measurements consisted of brightness comparisons of the pyrometer filament with various portions of the spectrum of the broad filament.

The spectral energy curve for the broad filament source was computed from its color temperature with the aid of Wien's equation in which C_2 was taken equal to 14,350 micron degrees. Correction for slit widths, for scattered light, for the absorption of the blue glass screen, and for the dispersion and selective absorption of the optical system of the apparatus were then made.

In Table I. the determinations have been reduced to a value of 100 at $\lambda = 450\,\mu\mu$. In this table are also included the visibility values of Nutting,[1] and Coblentz and Emerson[2] for the same range of wave-lengths. similarly reduced to a common value of 100 for $\lambda = 450\,\mu\mu$. It will be noted that the results here presented are lower in the extreme blue than those obtained from the data of Nutting, and Coblentz and Emerson.

With the data at hand one can compute for some definite temperature interval the effective wave-length of the blue glass screen mounted in the eyepiece. This was done for the temperature interval 1781° to 2475° K., and the value found by computation was $466.8\,\mu\mu$, while the experimental value found by Dr. Forsythe was $467\,\mu\mu$.

TABLE I.

Wave-lengths.	Mean Visibility of Twenty Subjects.	Mean Values Given by Nutting.[3]	Mean Values Given by Coblentz and Emerson.
410 $\mu\mu$	1.7	9.5	24
420	11.4	17.1	42
430	32.6	30.3	59
440	61.6	58.0	71
450	100	100	100
460	153	168	137
470	240	266	202
480	376	392	305
490	620	566	474
500	905	828	770

NELA RESEARCH LABORATORY,
NATIONAL LAMP WORKS OF GENERAL ELECTRIC CO.,
NELA PARK, CLEVELAND, O.

[1] Phil. Mag. (6), 29, p. 301, 1915 (corrected values).

[2] Bull. Bur. Stds., 14, p. 167, 1917.

[3] These values, kindly furnished by Dr. Nutting, differ slightly from his published data owing to a redetermination of the distribution of energy in the spectrum of the acetylene flame used.

Theory of Thermal Conductivity in Metals.[1]

By Edwin H. Hall.

IT is generally admitted that there are "free" electrons in the interatomic spaces of a metal and that their number per unit volume increases with rise of temperature. Hence there must be, in a detached metal bar hot at one end and cold at the other, a mechanical pressure tending to drive the free electrons down the temperature gradient. If this tendency prevails, even to a very slight extent, it makes the hot end of the bar electrically positive and the cold end negative.

If, now, some of the associated electrons are capable of progressive motion, from one atomic union to another during contacts, they will yield to the influence of the electric-potential gradient, whereas they will not be subject to the direct influence of the mechanical-pressure gradient. The result of the conditions described will be a constant procession of free electrons from the hot to the cold end of the detached bar and an equal procession of associated electrons from the cold to the hot end. These movements must be attended by a constant process of ionization, absorbing heat, at the hot end and a constant reassociation, releasing heat, at the cold end. That is, the free electrons will function like a vapor, and the metal bar will be somewhat analogous to the familiar Regnault apparatus for testing the boiling point of liquids, the hot end corresponding to the boiler and the cold end to the condenser, from which the liquid trickles back under the influence of gravity.

Doubtless a complete theory of the action in question must take account of ionization and reassociation at other points than the very ends of the bar; but, ignoring this complication for the present, we can get some notion of the possible heat-carrying power of the operations described by the following course of reasoning, partly conjectural:

The E.M.F. of a copper-iron thermoelectric couple for 1 degree temperature difference is about 1×10^{-5} volts at 20° C. Let us suppose that the contribution of the copper to this total is something between one quarter and one tenth of the whole, that is, something between 2.5×10^{-6} and 1×10^{-6} volts. Let us suppose, further, that the electric conductivity of copper is one half due to the associated electrons, so that the specific resistance, the associated electrons only being considered, would be about 3×10^{-6} ohms. These estimates give, as the magnitude of the constant electric current, in each direction, in a detached copper bar with unit temperature gradient, something between 0.83 and 0.33 ampere per sq. cm. of cross section.

If, now, we suppose that the ionizing heat corresponds to a potential difference of 5 volts, which seems a not unreasonable estimate from such data as we possess, we find that our apparatus should carry heat at a rate between 4.15 and 1.65 joules per second per sq. cm. of cross section. The known thermal conductivity of copper is about 1 calorie, that is, about 4 joules. No great

[1] Abstract of a paper presented at the meeting of the American Physical Society held in Pittsburgh, December 27–29, 1917.

importance should be attached to the closeness of the agreement here; but the calculation, uncertain though it be, is enough to show that the theory under consideration is worthy of further development.

CAMBRIDGE, December 26, 1917.

THE SIZE AND SHAPE OF THE ELECTRON.[1]

BY ARTHUR H. COMPTON.

IF the electron is sensibly a point charge of electricity, the mass absorption coefficient for X-rays and gamma rays should, according to classical theory, never fall below 0.188 in the case of aluminium. The experiments of Barkla with hard X-rays and of Ishino and others with hard gamma rays, show a value considerably less than this, falling as low as 0.045 when the penetrating radiation from radium C is used. Moreover, the scattered radiation from very hard rays should by classical theory be equally intense on the incident and the emergent sides of a plate through which the rays pass—a prediction contrary to the experimental observation that the intensity of the scattered radiation on the emergent side is much the greater.

These difficulties may be explained if the electron, instead of being a point charge, is considered to have a radius comparable with the wave-length of the incident beam. The scattering of gamma rays by electrons of appreciable diameter has been calculated, both on the assumption that the electricity is distributed in a spherical shell and on the ring electron hypothesis. Both types of electrons are found to be capable of explaining quantitatively the low absorption observed, with very short rays if the electron has a radius of about 2.5×10^{-10} cm. Such a large electron accounts also for the difference in intensity of the incident and the emergent scattered radiation, though the ring electron appears to give the better quantitative agreement in this case. The ring electron has the further advantage that it is capable of explaining A. H. Forman's observation that iron has a slightly greater absorption coefficient when magnetized parallel to the transmitted X-ray beam than when unmagnetized. This is due to the fact that when the axis of the ring is parallel with the incident X-rays, the energy scattered by the electron is a maximum. It appears probable, therefore, that the electron consists of a ring of electricity whose radius is about 2.5×10^{-10} cm.

RESEARCH LABORATORY,
WESTINGHOUSE LAMP CO.,
December 15, 1917.

CHARACTERISTIC CURVES OF VARIOUS TYPES OF AUDIONS.[1]

BY A. D. COLE.

THIS paper presented the general results of a study of the change in the value of the plate current and the grid current of an audion tube as the

[1] Abstract of a paper presented at the meeting of the American Physical Society held in Chicago, December 1, 1917.

following factors were varied: viz., the P.D. between filament and grid, the P.D. between filament and plate, the magnitude of filament current, magnitude of received signal, type of signal source, kind of audion used and closeness of coupling in the sending signal circuit.

Seven different types of audions were used and three kinds of signals. In each experiment, with other conditions fixed, the P.D. between the negative end of the filament and the grid was varied step-by-step by a potentiometer arrangement and the value of both plate-current and grid-current noted for each step. These current values were plotted. At each step it was noted how much the value of each of the currents was changed when an incoming signal superposed an alternating P.D. upon the D.C. voltage corresponding to that step. These current changes were plotted as "plate-signal" and "grid-signal" curves.

Diagrams were shown for the set-ups used for different types of signals. The kinds of signals used were waves from a neighboring high-frequency oscillating audion circuit, waves of same frequency from a buzzer circuit and low frequency from a 60-cycle A.C. source.

About a dozen lantern slides and charts were shown, each giving a typical group of the four characteristic curves, plate-current, grid-current, plate-signal and grid-signal.

OHIO STATE UNIVERSITY,
December, 1917.

THE EFFECT PRODUCED UPON AUDION CHARACTERISTIC CURVES BY VARIOUS KINDS OF SIGNALS (BUZZER, ELECTRON RELAY AND 60-CYCLE A.C.).[1]

BY A. D. COLE.

THE present study is a continuation of the work reported upon at the Chicago meeting of the American Physical Society under the title "Characteristic Curves of Various Types of Audions." Three of the seven types of audions included in the earlier study were particularly examined to find how much the magnitude of the plate signal and the grid signal depend upon the kind of excitation used. The terms plate signal and grid signal are used in the sense defined by Dr. L. W. Austin in a recent paper;[2] viz., the changes in the magnitude of the plate current and grid current produced by the momentarily applied alternating E.M.F. It was found that the magnitude of the effect, its law of change with variation of the D.C. voltage applied to grid and even its sign were different, according to whether the signal E.M.F. was produced by a buzzer, an oscillating audion or 60-cycle A.C. source. But the kind of variation was different in different types of audions. For example in an "oxidized-filament" De Forest bulb, excited by high frequency signals

[1] Abstract of a paper presented at the meeting of the American Physical Society held in Pittsburgh, December 27–29, 1917.

[2] Radiotelegraphy—Notes on the Audion; L. W. Austin, Jour. Wash. Acad., Vol. 7, No. 15, Sept., 1917.

of about 2,000 meters wave-length from another audion, the plate-current curve, grid-current curve and grid-signal curve were normal and similar to those shown in the figure of Dr. Austin's paper above referred to; the ordinate of the plate-signal curve changed sign at the usual place, but positive values were unusually small and negative values unusually large. With buzzer excitation, however, positive values were relatively larger, the change of sign occurred later, and negative values never exceeded the positive; the form of the grid-signal curve was peculiar, with large positive values throughout the entire range of D.C. voltage used. The 60-cycle excitation gave a form of plate-signal curve different from either, the ordinates never becoming negative; its grid-signal curve was much like that obtained with the buzzer.

With a Western Electric audion of cylindrical pattern, both high-frequency audion and 60-cycle sources gave plate-signal and grid-signal curves slightly abnormal but much alike. The buzzer curves, however, were quite different; the ordinates of the plate-signal curve changed sign at the usual place, but positive values gave a curve with remarkably flat top, while the negative were larger with the usual well-marked maximum. The grid signal showed large positive values throughout the entire voltage range used.

Similar curves were shown and comparison made between the same three kinds of excitation for De Forest Hudson-filament bulbs. High-frequency audion and 60-cycle excitation gave similar signal curves, all quite normal. But here also the buzzer excitation gave signal curves that were both quite far from normal, and also different from those obtained from the other types of tube.

This work was done at the U. S. Naval Radio laboratory at the suggestion of its Director, Dr. L. W. Austin, and the resources of his laboratory generously placed at the author's disposal. The work is being continued at the Ohio State University. A full description accompanied by many curves will soon be published, probably in the Proceedings of the Institute of Radio Engineers.

OHIO STATE UNIVERSITY,
December, 1917.

REPORT ON THE CONSTRUCTION OF CERTAIN MATHEMATICAL TABLES.[1]

BY C. E. VAN ORSTRAND.

The following tables are ready for publication.

TABLE I.—Values of $y = \frac{2}{\sqrt{\pi}} \int_0^x e^{-x^2} dx$ ranging from 5 to 8 places of decimals at intervals of 0.0001 from 0.0000 to 3.0000.

TABLE II.—Inverse values of $y = \frac{2}{\sqrt{\pi}} \int_0^x e^{-x^2} dx$ to 5 places of decimals at intervals of 0.0001 from 0.0000 to 0.9000 and at intervals of 0.00001 from 0.90000 to 1.00000.

[1] Abstract of a paper presented at the meeting of the American Physical Society held in Pittsburgh, December 27–29, 1917.

TABLE III.—Values of the reciprocal of $n!$ to 108 places of decimals at intervals of unity from 1 to 74.

TABLE IV.—Values of e^x to 42 significant figures at intervals of unity from 0 to 100.

TABLE V.—Values of e^x to 33 significant figures at intervals of 0.1 from 0.0 to 50.0.

TABLE VI.—Values of e^x to 62 places of decimals at decimal intervals from 1×10^{-10} to 9×10^{-1}.

TABLE VII.—Values of e^{-x} ranging from 52 to 62 places of decimals at intervals of unity from 0 to 100.

TABLE VIII.—Values of e^{-x} ranging from 33 to 48 places of decimals at intervals of 0.1 from 0.0 to 50.0.

TABLE IX.—Values of e^{-x} to 63 places of decimals at decimal intervals from 1×10^{-10} to 9×10^{-1}.

TABLE X.—Values of $e^{\pm(n\pi/360)}$ to 23 places of decimals or significant figures at intervals of unity from $n = 0$ to $n = 360$.

TABLE XI.—Values of $e^{\pm n\pi}$ to 25 places of decimals or significant figures for various values of n.

TABLE XII.—Values of sin x and cos x to 23 places of decimals at intervals of unity from 0 to 100.

TABLE XIII.—Values of sin x and cos x to 23 places of decimals at intervals of 0.1 from 0.0 to 10.0.

TABLE XIV.—Values of sin x and cos x to 23 places of decimals at intervals of 0.001 from 0.000 to 1.600.

TABLE XV.—Values of sin x and cos x to 25 places of decimals at decimal intervals from 1×10^{-10} to 9×10^{-4}.

TABLE XVI.—Miscellaneous values of e^x, e^{-x}, sin x and cos x to a great number of decimals including Boorman's value of e.

TABLE XVII.—Values of sin θ and cos θ to 28 places of decimals for various values of θ expressed in seconds.

U. S. GEOLOGICAL SURVEY,
WASHINGTON, D. C.

THE OPTICAL PROPERTIES OF RUBIDIUM.[1]

BY J. B. NATHANSON.

THE optical constants of rubidium were obtained for wave lengths ranging from 454.6 $\mu\mu$ to 640.9 $\mu\mu$. A simple Babinet compensator and two nicols were employed to measure the phase difference and azimuth. The constants were calculated by means of Drude's formulæ.

The rubidium mirror was formed by distillation of the metal in an atmosphere of rarified nitrogen, with subsequent condensation upon a piece of plane parallel glass. A right angle prism served to eliminate the troublesome reflections from the glass front of the mirror.

[1] Abstract of a paper presented at the meeting of the American Physical Society held in Pittsburgh, December 27–29, 1917.

The coefficient of absorption was found to vary from 5.28 for $\lambda = 454.6\,\mu\mu$ to 10.51 for $\lambda = 640.9\,\mu\mu$. There was only a very slight variation in the value of the index of refraction which was equal to about 0.14.

The reflecting powers of the rubidium in contact with glass varied from 74.5 per cent. for $\lambda = 454.6\,\mu\mu$ to 82.7 per cent. for $\lambda = 640.9\,\mu\mu$. These values are (with the exception of that for $\lambda = 589.3\,\mu\mu$) somewhat lower than those obtained directly by means of a photoelectric cell in a previous investigation.[2]

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[2] Astrophysical Journal, 44, 137, 1916.

NEW BOOKS.

Table of Log_{10} Sec^2 θ. By P. S. HELMICK. 16 pp. Published as University of Iowa Monograph No. 4. 1917.

This table is intended for use with photographic density apparatus employing nicol prisms in their construction, and gives the photographic density of the plate, *i. e.*, $\text{Log}_{10}\left(\frac{\text{Incident Light}}{\text{Transmitted Light}}\right)$, directly in terms of the angle of rotation of the nicols. The value of the function is given every 0°.05 from 0° to 89°, and every 0°.01 from 89° to 90°, together with the tabular difference for each 0°.01 for the whole range. The table may be obtained on request from The Librarian of the State University of Iowa, Iowa City, Iowa.

A College Text-Book of Physics. By ARTHUR L. KIMBALL. New York: Henry Holt and Company, 1917. Second edition, revised. Pp. x + 694.

In the six years since the publication of the first edition this book has enjoyed a well-merited success, due especially to its emphasis on the physical rather than the mathematical side of the subject. In clarity and exactness it compares favorably with most existing texts. The reviewer is among those friends of the book who had hoped that its favorable reception would have encouraged the author to make more radical departures from convention when revising for the new edition, in order to make the treatment still more aggressively physical. In this respect we are disappointed, as the new edition shows only minor changes. A few paragraphs rewritten to bring them up to date, amplification of the treatment of wireless telegraphy and telephony—these are changes that could have been predicted. The new section on the flicker photometer does not seem to fill any crying need and could have been omitted without detriment. There are two appendices, one on Carnot's cycle and the other a proof of Newton's wave formula. The first of these should have been incorporated in the text. A very genuine and substantial improvement is effected in the arrangement of the chapters on mechanics by placing the sections on statics earlier. The substitution of the elements of electron theory for those of displacement theory is also to be commended, as well as the improvement in the definitions of the electrical units.

The weakest part of the book is its collection of problems. The great merit of the text treatment is its emphasis on physical rather than mathematical reasoning; but when we turn to the problems we find for the most part a rather conventional collection of numerical examples of the formula-substituting kind. The evil is exaggerated in some cases by giving unproved formulas in the text, and then problems requiring the use of such formulas. As an instance,

we may cite the formula for the speed of water waves, or the formula for the force with which a magnet holds its armature. It is of small advantage to avoid the use of mathematics as an instrument of reason if the student is to be thus encouraged to use it as an instrument for avoiding thought. A larger number of problems of a kind incapable of numerical solution would be much more to the author's purpose.

One or two errors of fact may be noted. The meter is defined in terms of the *mètre des archives* instead of the International Prototype Meter, and the metric equivalents of the English foot and yard are given where the American standards would be better. In Article 146 it is stated that the spin of a shell causes it to keep pointing in a nearly constant direction in spite of air resistance. The facts appear to be that *because* of air resistance the axis of the shell keeps parallel to the trajectory. A spinning shell mounted on gimbals has been found to turn its nose into a blast of air. The Leyden jar with removable coatings reappears and seems hard to get out of our texts, in spite of the fact that the whole phenomenon depends on the heterogeneity of the dielectric.

The comparative triviality of these blemishes serves only to emphasize the accuracy of the text as a whole.

C. M. S.

Organic Evolution. By RICHARD S. LULL. New York: Macmillan Company, 1917. Pp. xviii + 729. Price, $3.00.

This textbook (designed for use in college courses) gives an account of the principal theories advanced to explain the existence of the various species of plants and animals. It contains many interesting facts relating to the physical and chemical properties of protoplasm, and to the extraordinary mechanisms by which organisms nourish themselves and reproduce their kind.

In the last two thirds of the book the evidences of organic evolution are presented, especially those derived from paleontology. This section closes with interesting statements concerning the evolution of man.

A physicist cannot help being struck by the number of far-reaching generalizations that have been deduced in this branch of science from what appears to him to be very meager non-quantitative evidences.

Students of physical science who are interested in the development of biophysics will find the book very useful and suggestive.

W. D.

Building Human Intelligence. By DR. ARNOLD LORAND. Philadelphia: F. A. Davis Co., 1917. Pp. xii + 451. (*Received.*)